ARMY RESEARCH LABORATORY

Assessment of Paint Layers by FE-SEM and EDS Examination

by Donovan Harris

ARL-TR-3232 June 2004

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14. ABSTRACT
Three painted aluminum panels were examined to verify total coating thickness and to determine the thickness of each coating layer. The approach was to remove free-film samples from each panel, fracture the films, and then examine at high magnification the cross sections using a field emission-scanning electron microscope (FE-SEM). The initial film removal method was not successful. It was decided to back-score a section of each panel and then freeze-fracture a whole segment. The FE-SEM micrographs confirmed the thickness measurements made earlier using an Elcometer. The observed morphology of each coating film was consistent across the entire thickness, and no layering could be determined. Energy dispersive spectroscopy was used to analyze each film and then map the elemental distributions across each film thickness. The use of quantitative elemental mapping showed the actual chemical distributions and indicated the presence of two distinct layers. On each panel, one layer accounted for a minimum of about two-thirds of the total thickness of the paint film, but both layers were the epoxy primer. No discrete chromate layer was detectable.

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FE-SEM, element mapping, paint films, uncoated, layer analysis

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1. Introduction

A number of 12- × 4- × 1/4-in aluminum panels were first treated with a chromate conversion coating, DOD-P-15328,[1] and then were primed using MIL-P-53022.[2] The coating process occurred at another site, and the panels were then sent to the U.S. Army Research Laboratory, Aberdeen Proving Ground, MD for testing. The panels were artificially aged using several exposure techniques. During the exposure testing, several panels experienced blistering or loss of adhesion, which is usually a result of the coating film being too thick. The panel film thicknesses were measured using an Elcometer, and total thicknesses were found to exceed the combined total allowed under the two governing specifications. The application facility felt that could not be the case. A physical confirmation of the coating thickness and layer thicknesses was needed. The panels to be evaluated had been prelabeled 2, 5, and 7 as part of the original coating process.

2. Procedure

One area where the coating was the thickest was scored to form a series of squares. The panel was immersed in liquid nitrogen for 1 hr. A micro angled-chisel-point X-acto* blade was tried to penetrate a film edge and pop free a square of film. The chisel angle of the tip was too large for the task.

It was then decided to back-score the width of the panel and freeze-fracture off a 1/4- × 4-in-long strip of panel. The panels were scored by hand using an Atlas model rail saw. The depth of the score appeared to be half the panel thickness, and starter cracks were cut in at each end of the strip. This approach was used to avoid overheating the film and to minimize possible contamination. The panels were individually immersed for 1 to 2 hr before fracturing. The fracture results for each panel produced a result that was unique to it. The panel order for fracturing was 5>2>7, which is in descending order of measured film thickness. As shown in figure 1, the back scoring penetrated less than half the panel thickness, and then only for the deepest scored panel (panel 7).

Panel 5 was scored the shallowest, so instead of fracturing free, the strip twisted and buckled. That action caused large sections of the coating film to pop free, which were captured in a plastic container. Panel 2 was cooled for 90 min instead of 60, before fracturing. This time, force was

[1] DOD-P-15328. Primer (Wash) Pretreatment.

[2] MIL-P-53022. Primer, Epoxy Coating, Lead and Chromate Free.

* X-acto is a trademark of Hunt Mfg. Company.

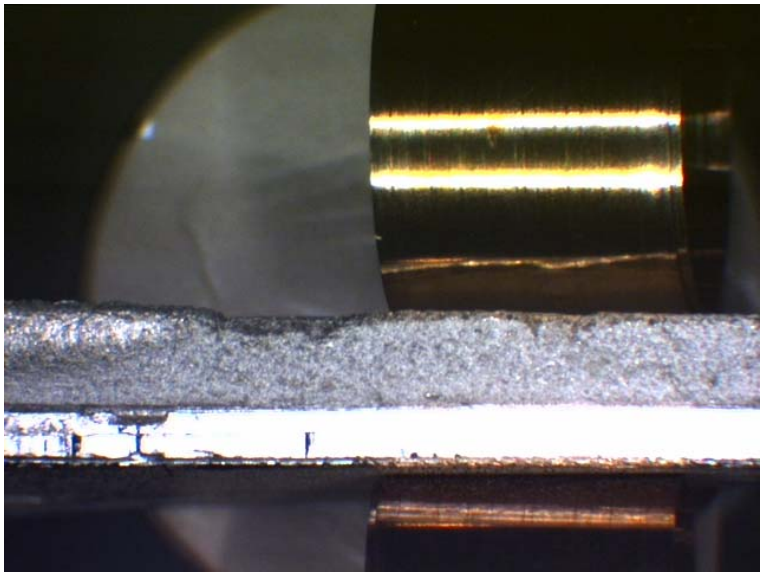

Figure 1. Panel 7 fracture face. Coating film is the thin light line across the upper quarter of the field. The thick bright bar running across the lower portion is the back-scored area.

applied in a way to force twisting and buckling in the scored strip. The free-film segments produced were substantially smaller than those from panel 5 were, but readily usable. While panel 2 was being cooled, panel 7 was scored still more and the two starter cracks cut longer. Panel 7 was then cooled for 2 hr before fracturing. The technique used with panel 2 did not produce any useful free-film segments. The scored segment actually fractured in part, so the panel was rechilled for 30 min, then fractured some more and rechilled again before the fracturing was completed. That process did not leave a clean-coating fracture edge along the panel fracture edge. The net results for panel 7 were no usable free films and film cross sections were only randomly available.

The free films were mounted using metal spring clips, and then the clips were attached to 15-mm stubs using conductive silver adhesive (figures 2 and 3). The silver adhesive was cured for 80 hr before observation in a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). These clips have previously proven successful in imaging uncoated free films with the FE-SEM (figure 4). The strip from panel 7 was mounted using a spring loaded vise clamp mount.

3. Instrumentation

A Hitachi S-4700 FE-SEM, having a yttrium aluminum garnet (YAG) backscatter detector (YAGBSE) and two (upper and lower) secondary electron (SE) detectors, was used for morphological analysis of the samples. An Edax HIT 4700(II) detector with an ultra-thin

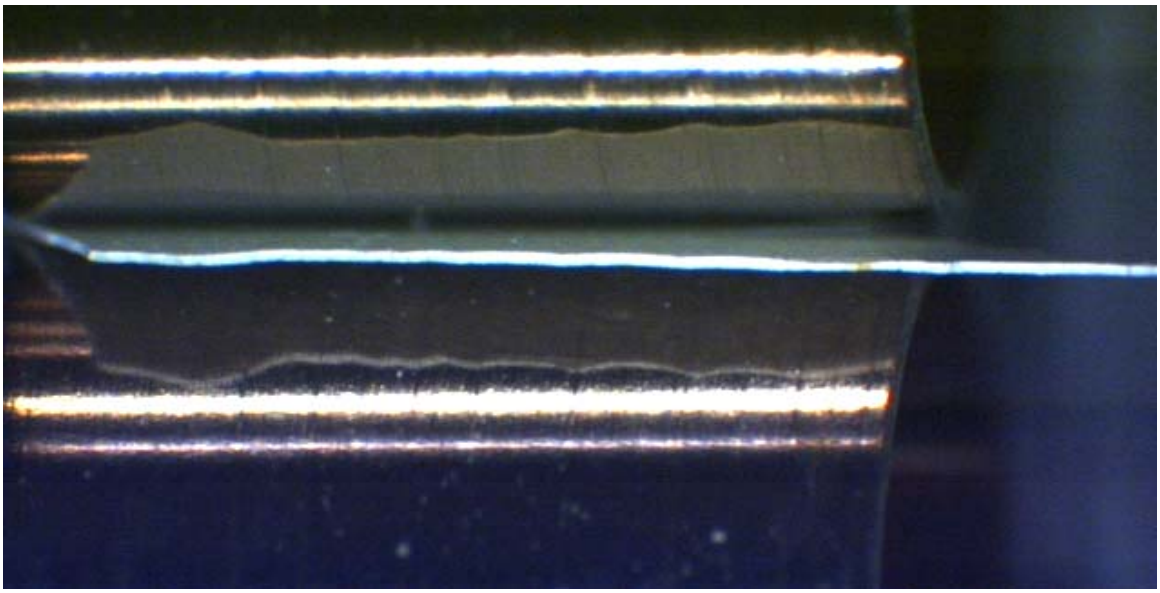

Figure 2. Panel 5 free film in metal spring clip.

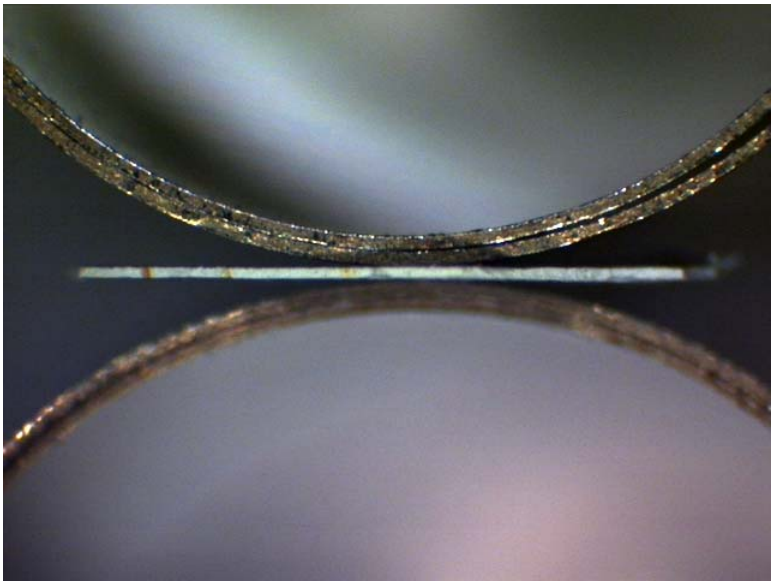

Figure 3. Panel 2 free film in metal clip at 10×.

window, resolution 133 eV, provided the energy dispersive spectrometer (EDS) capability for the Hitachi.

4. Analysis of Coating Films

The samples were not coated to make them conductive and possibly obscure any layer transition morphology changes. The vise-mounted sample from panel 7 was examined first, as that contact

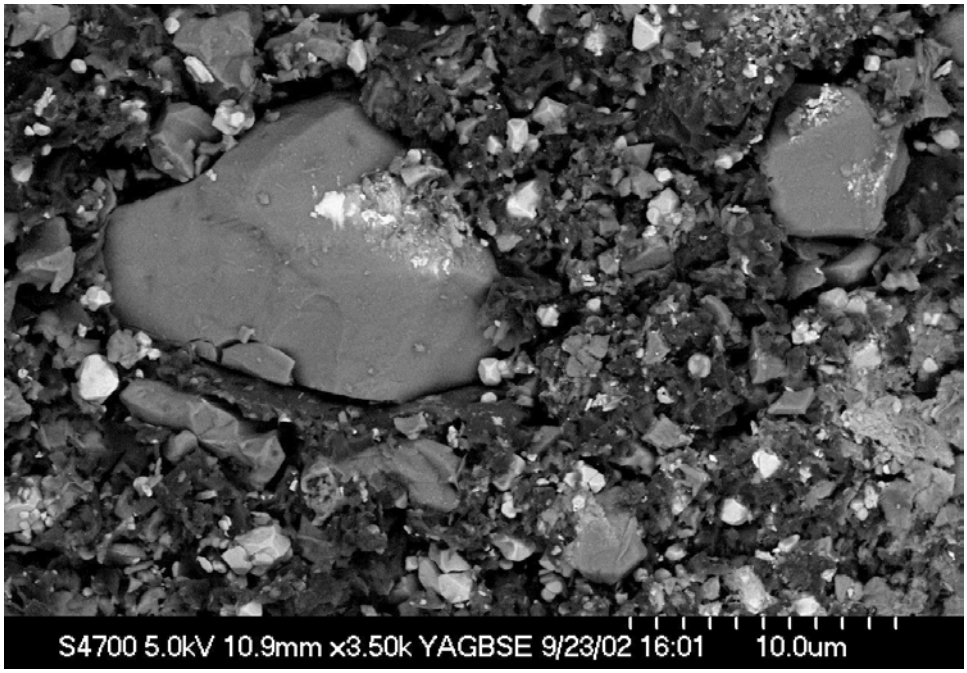

Figure 4. Previously examined coating free film using the S-4700 and metal spring clips. The free film had not received any type of conductive coating to reduce charging. This micrograph was taken using a YAG backscatter detector, and not the SE detector.

with two aluminum surfaces should improve the surface electron drain. Because of random charging with increased magnification, mixed signal SE was abandoned in favor of the lower detector. The YAGBSE detector provided improved details in the 2–10 KX range. Not having fully adequate electron drain limited the useful magnification to an upper limit of 18 KX, but did allow for the quantitative elemental mapping across the full cross section of each film sample later. Due to the 18-KX limit, morphology changes in the interface regions could not be observed. The Edax system was employed to see if an element was present in one portion of the coating and not the other, or if elements were present in significantly different concentrations across the film thickness. The order of analysis for the paint films was panel 7, 5, 2, for the morphology and then 7, 5, 2, plus panel 7 for the EDS.

5. Results

5.1 Morphology – All Panels

The segment from panel 7 could not be oriented to properly image the film cross section at higher magnifications above 1 KX. The way the surface coating shattered (figure 5) added to the orientation problem by inhibiting some surface electron drain, thereby increasing the surface charging at higher magnifications.

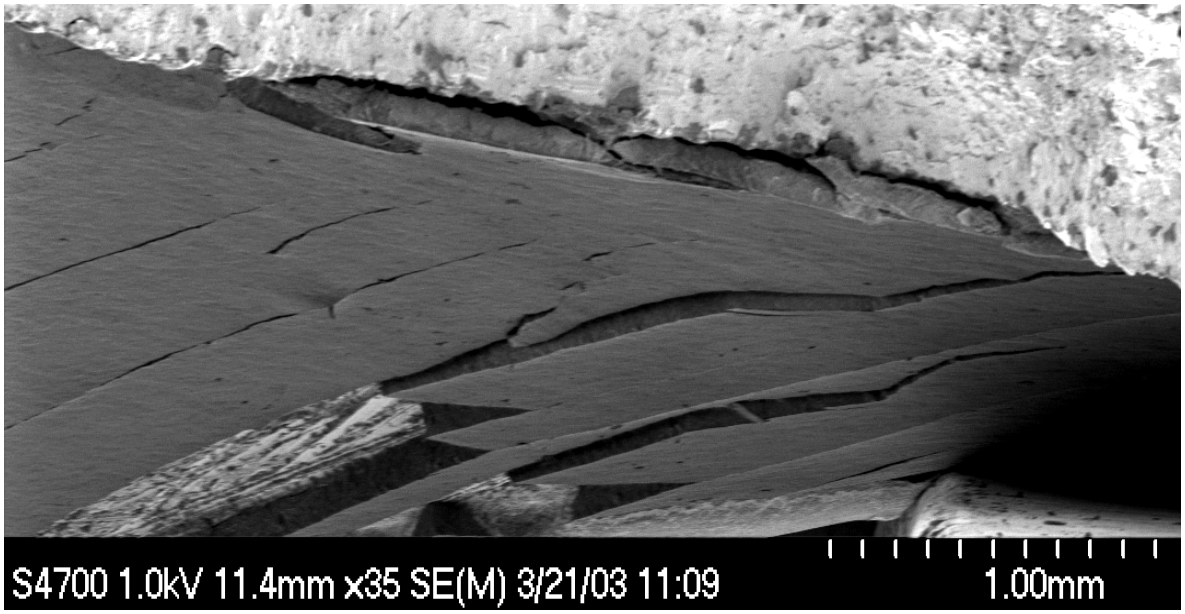

Figure 5. Panel 7 at 35× FE-SEM. Coating film is the darker area.

Figures 6 and 7 complete the available morphology documentation from panel 7. Note in figure 7 that only a portion of the surface is in clear focus. The film edge being imaged is below the panel fracture edge, and the size of both the vise mount and the panel strip limited stage tilt, so it was not possible to clearly focus the entire depth or width of the film thickness.

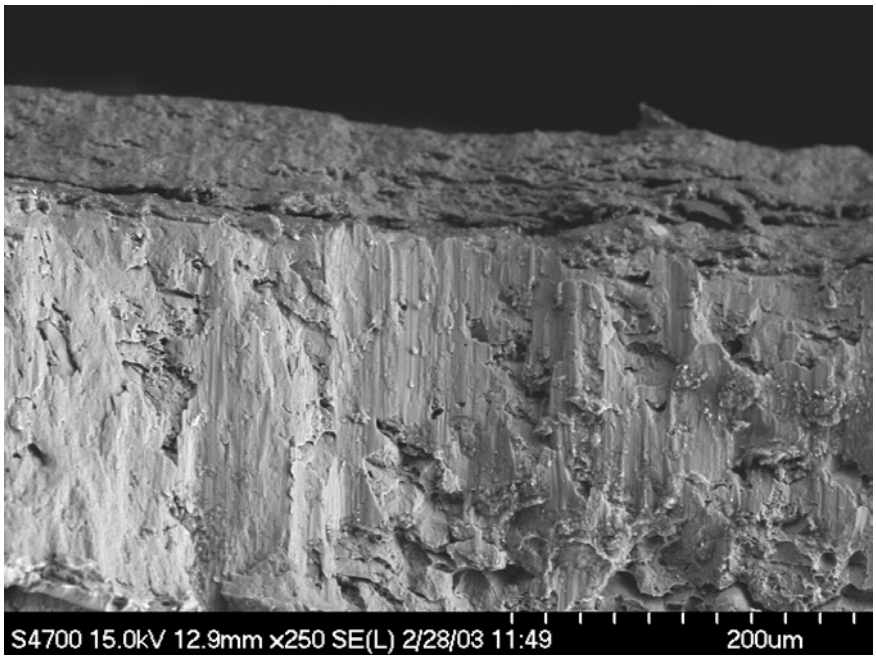

Figure 6. Lower SE detector image of panel 7 strip, light gray area, and coating, thin dark gray area.

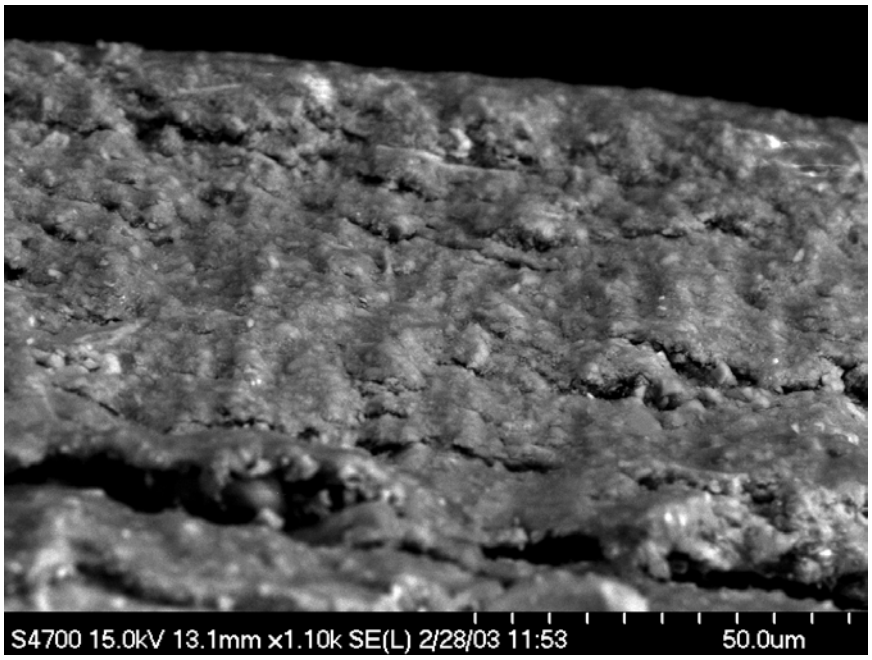

Figure 7. Lower SE detector image of panel 7 coating with aluminum panel (foreground).

The free film from panel 2 provided nearly all of the morphological data analyzed. As shown in figure 3, the film sample sits above the metal clip and is nearly contained by the clip. Most of the micrographs are located in the central area immediately adjacent to the clips, which has little influence on the surface charging. Figure 8 shows the film imaged using mixed SE detectors, while figure 9 is the same area imaged using the lower SE detector.

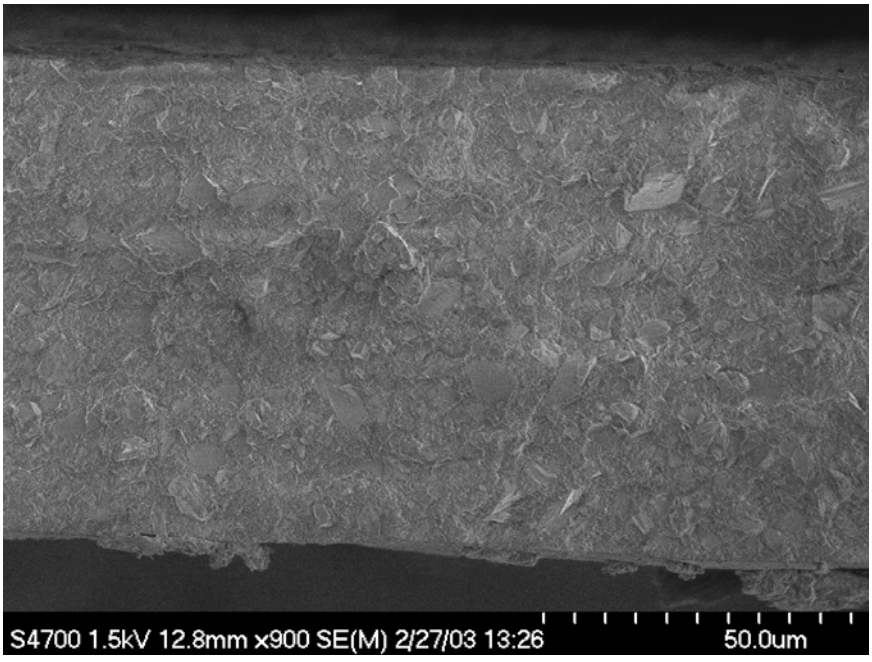

Figure 8. Panel 2 film using mixed SE detectors.

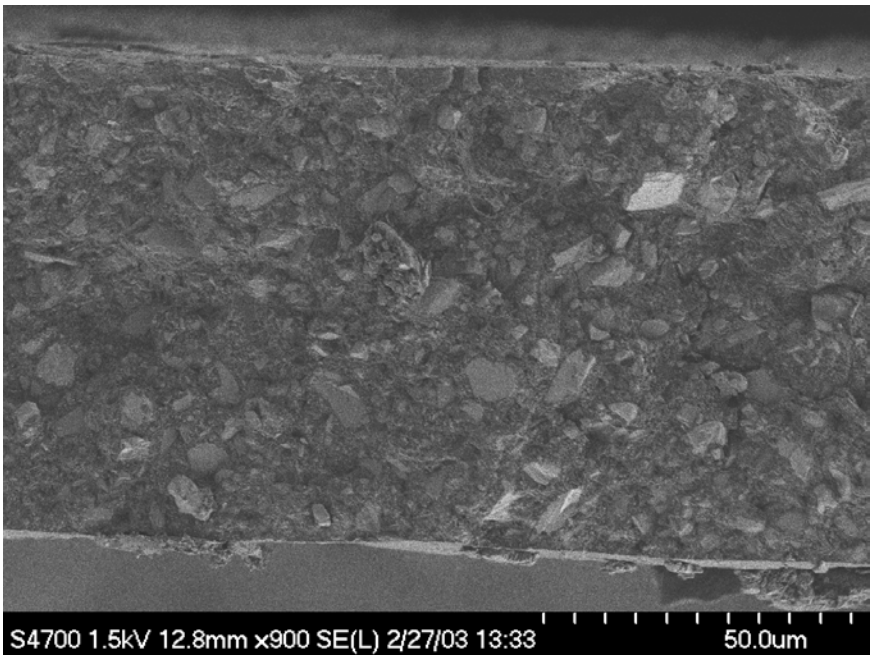

Figure 9. Panel 2 film using only the lower SE detector.

At 5 KX, the lower SE detector has a reduced resolution (figure 10), while the YAGBSE (figure 11) provides a clearer image even with charging present.

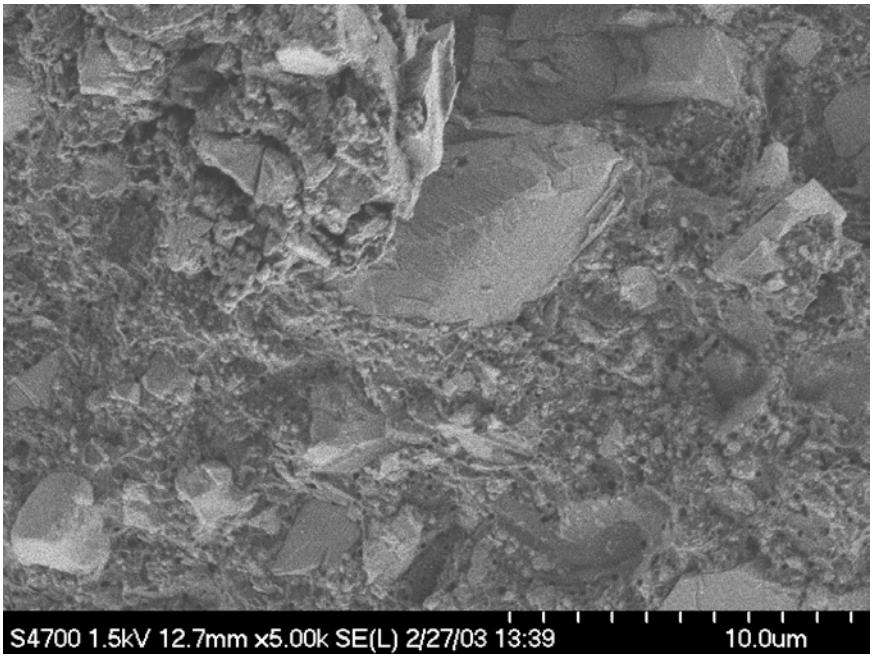

Figure 10. Lower SE detector image of film from panel 2.

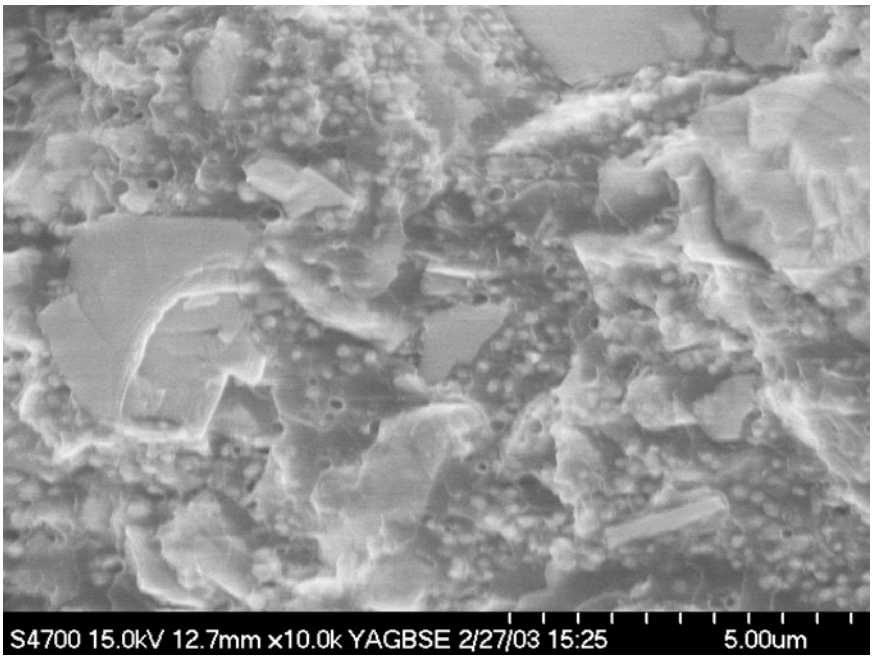

Figure 11. YAGBSE image of film from panel 2.

That clarity is reduced by charging at 10 KX (figure 12). Above 10 KX, charging became a problem. The 10-KX image was focused and stigmated at 18 KX, and a series of overlapping micrographs was taken to fully document the cross-section morphology of the film.

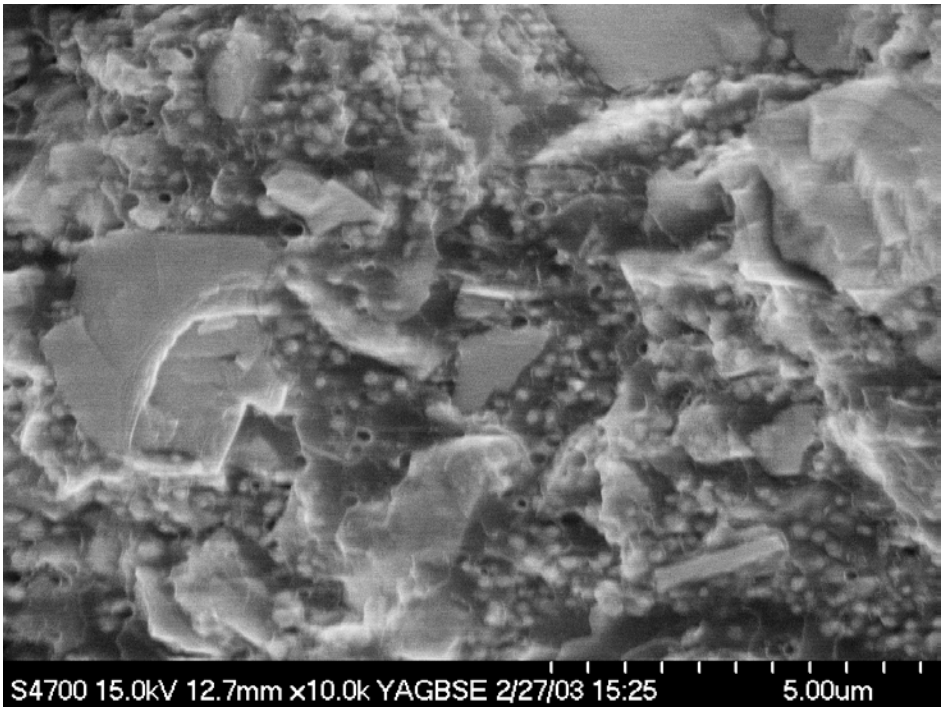

Figure 12. Panel 2 film YAGBSE image at 5 KeV.

The effects of acceleration voltage and surface roughness on the YAGBSE detector are seen in figures 13 and 14. These last two micrographs were taken from an area out on one of the "wings" of the sample, distant from the clip contact area, and at a source emission current of 2 μA. All the morphology micrographs are at 1- or 2-μA source emission current.

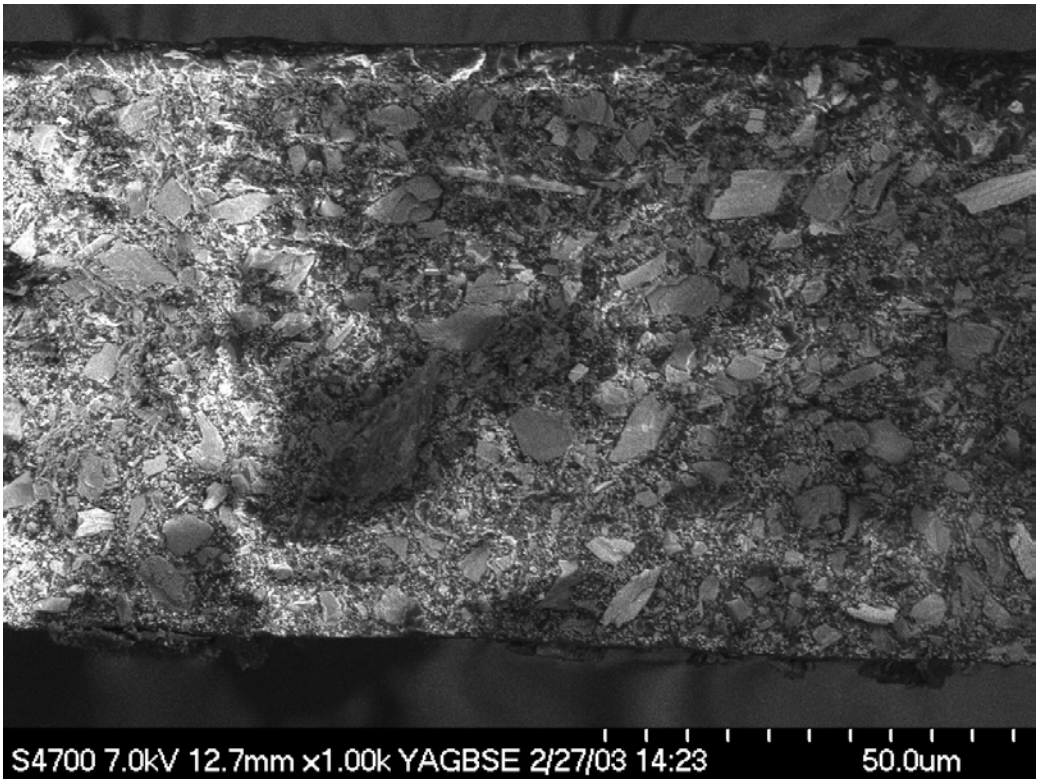

Figure 13. Panel 2 free film, YAGBSE, 1 KX, 7 KeV.

The free film from panel 5 extends high beyond the clip, as shown by figure 3. That sample placement produced the images in figures 14–16.

The clarity of the micrographs precludes identifying layer changes, but is sufficient to confirm that the Elcometer thickness readings are accurate. The film thicknesses were measured post-process using National Institutes of Health's Image J software on a PC.

5.2 EDS Analysis

The Edax Genesis software has three elemental mapping modes: Live, Standard, and Quantitative (Quant). In the Live mode, the dwell time is that time required to scan/capture one entire frame, 256 × 200 pixels for most of this study. The results from each frame scan can be added together. Most Live results are builds of 32 frames. In both the Standard and the Quant modes, the dwell time is the time the beam scans each pixel. With a 500-ms dwell time, a 256 × 200 pixel frame requires 8 hr to complete, or 5.5 hr at 400 ms. A frame of 128 × 100

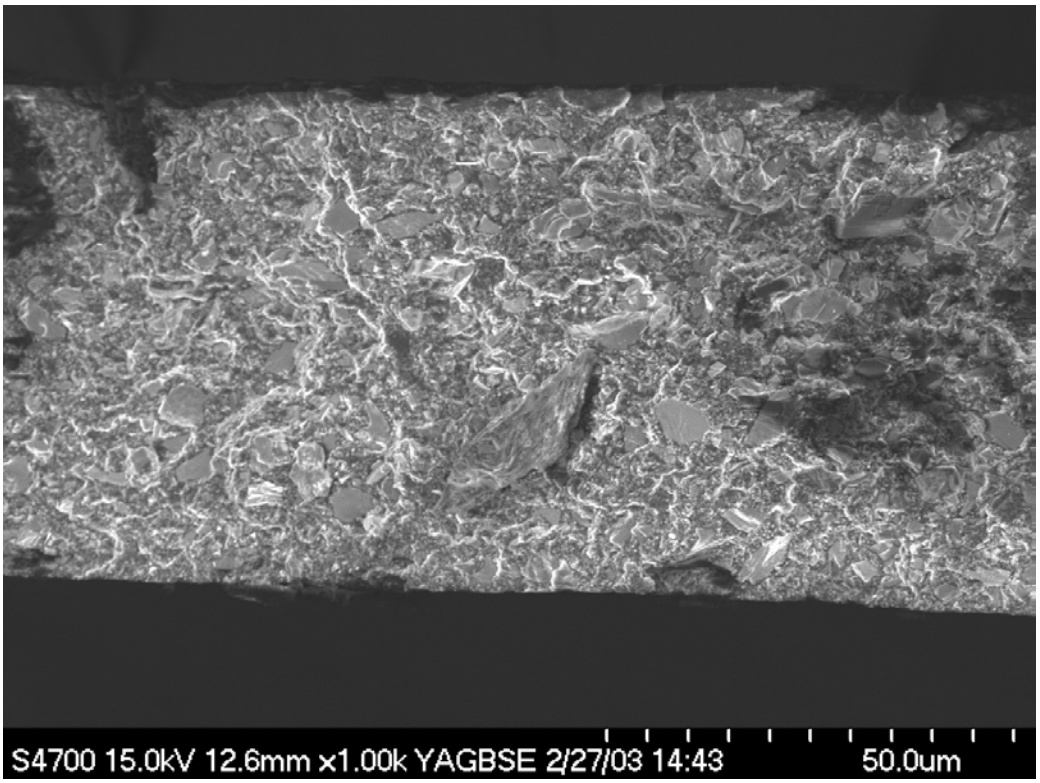

Figure 14. YAGBSE image at 15 KeV. Note charging.

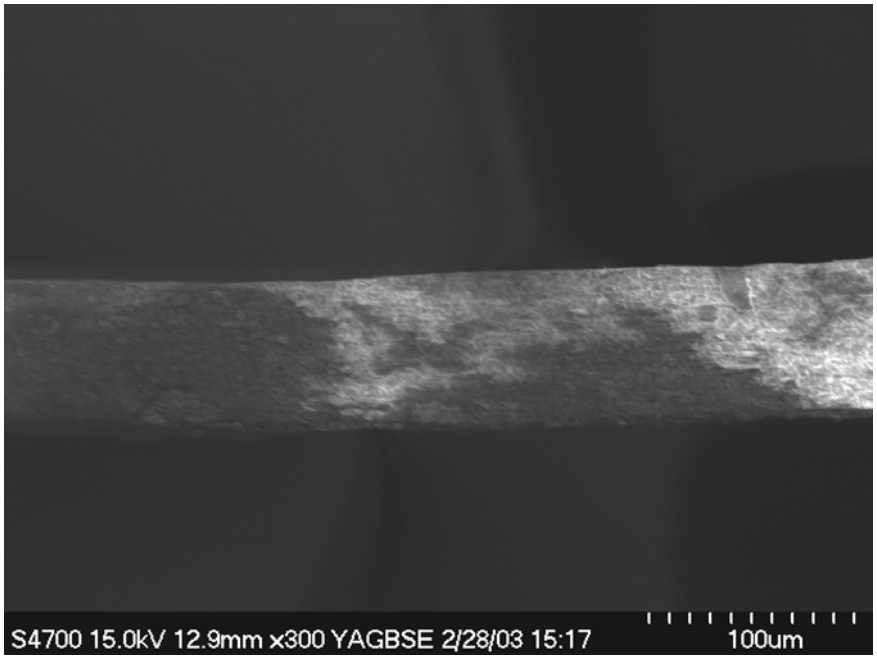

Figure 15. Panel 5 free-film 300× YAGBSE image.

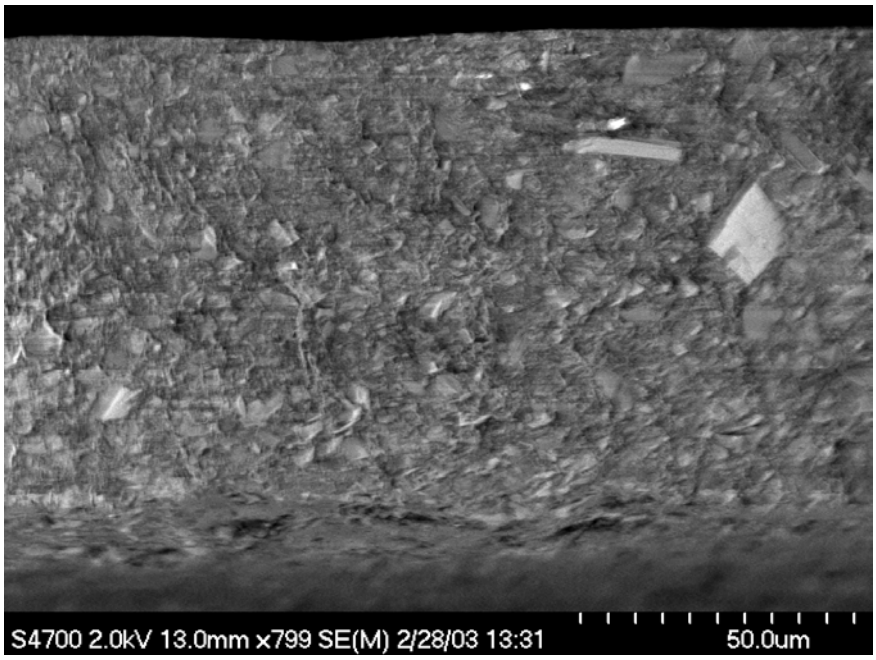

Figure 16. Panel 5 free-film 800× SE image.

pixels was used for all the Quant mapping done, with a ZAF weight-percent correction for each pixel. Except for the map of the aluminum, dwell times were 350–400 ms. The aluminum panel was Quant mapped using a 250-ms dwell time.

5.2.1 Panel 7 EDS

As noted earlier, the frame of the vise holder was too large to allow stage rotations greater than ±5° or tilts >10°. The 4-in sample width limited the viewable area to the middle 2 in of the sample. The spectrum in figure 17 was taken from the area shown in figure 18.

Then a Live elemental map was captured at 500-ms dwell time/frame of 256 × 200 pixels. The spectrum and mapping were performed at 15-KeV and 10-μA emission current. The elemental maps were allowed to build so that titanium distributions were readily evident. Figure 19, Live map 01, is at 1.5 KX, and figure 20, Live map 03, at 2 KX. Comparing the two Al K maps shows an alignment error between the S-4700 and the EDAX external control module. Note the total absence of a chromium response. Because of the sample handling problems and the failure to see any changes in distribution with the panel 7 sample, it was decided to work with the free film from panel 5.

5.2.2 Panel 5 Free Film

The free film from panel 5 was chosen to establish the Quant mapping parameters, solely due to the large cross-sectional area available. Initially, the sample was mechanically oriented along the x-axis. Because of some unexplained peaks, the stage was rotated so that the sample was aligned along the y-axis, with the clip above the sample and away from both the beam and the

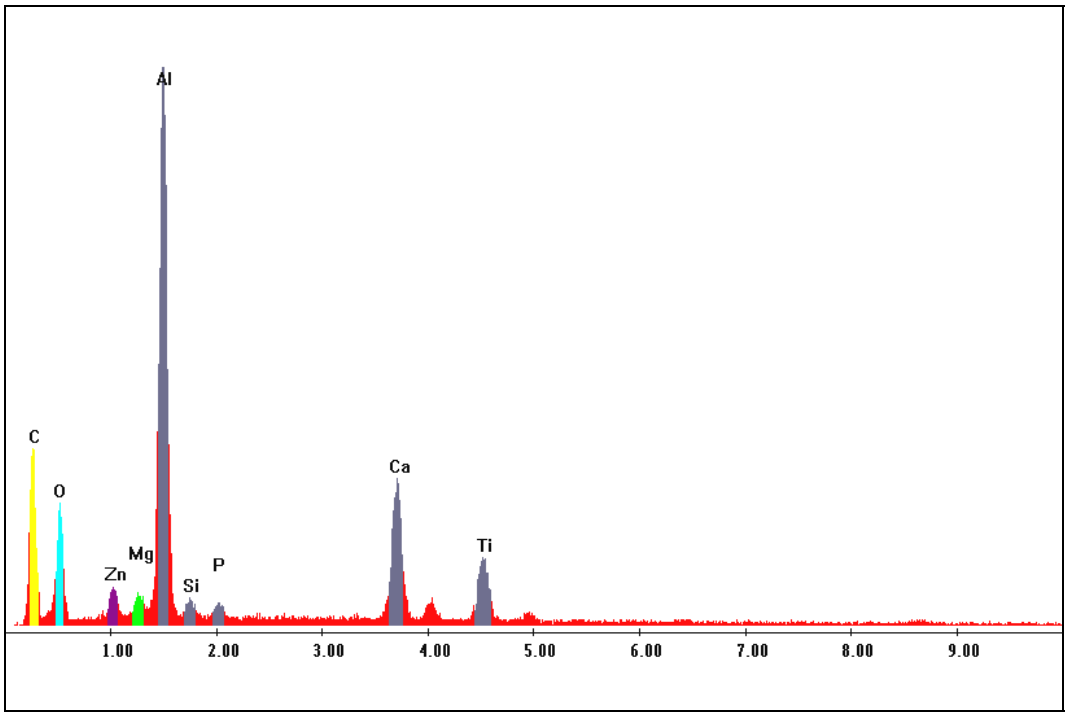

Figure 17. Spectrum for area in figure 18.

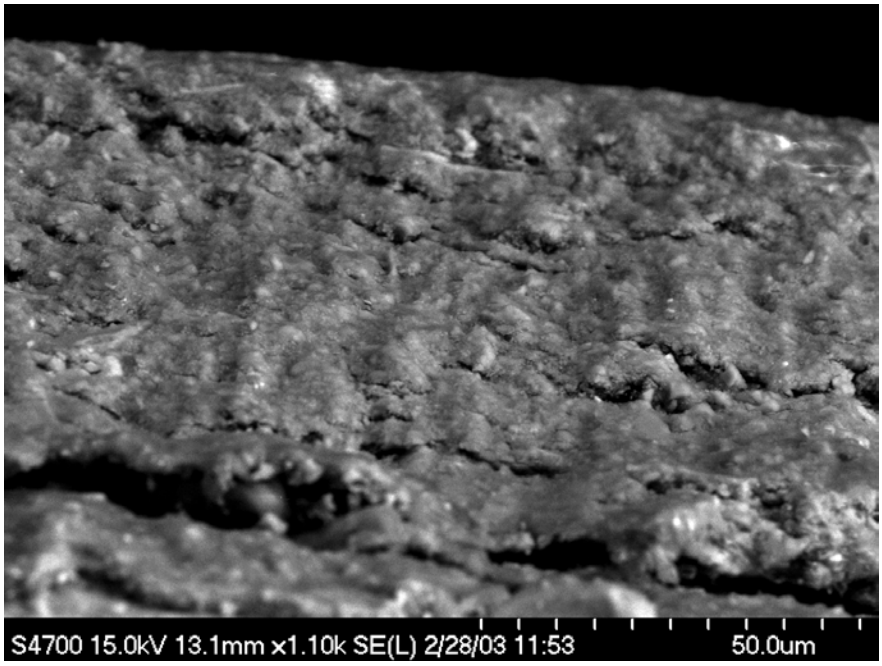

Figure 18. 1-KX image. Note lack of focus due to tilt.

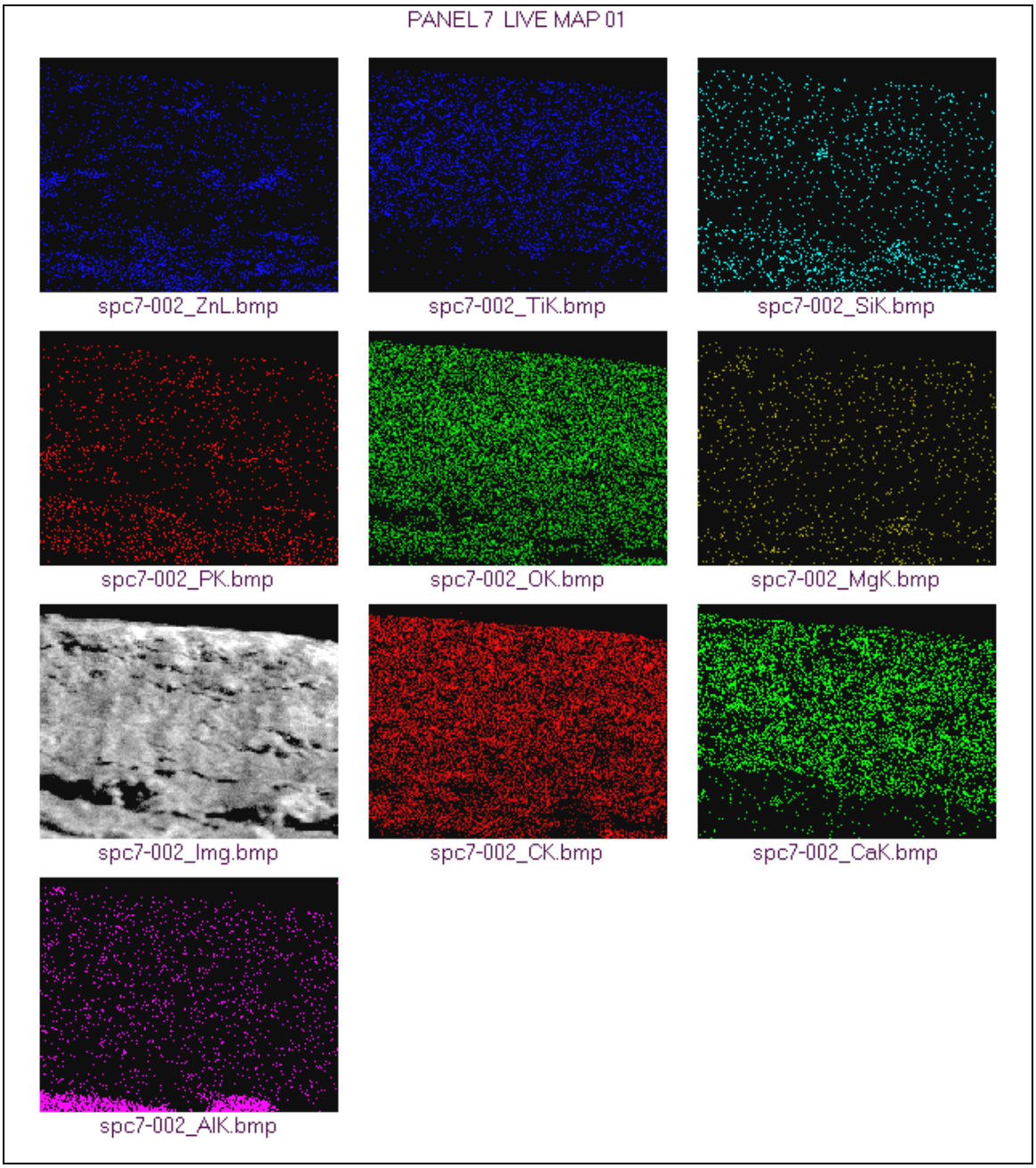

Figure 19. Live map of panel 7 film at 15 KeV and 1.5 KX.

EDS detector. Figure 21 shows the results of a Quant elemental mapping of the free film oriented along the x-axis. The beam was 20 KeV with a 10-μA emission current. The mapping was done with a 400-ms dwell time and a 128 × 100 pixel frame. The Zn K map reveals the presence of a number of large clusters. The apparent V K response is really a Ti Kβ response installed by the auto ID function. The bright solid band in the O K response is not readily explained, especially in the absence of any visible charging on the image map. The Fe K

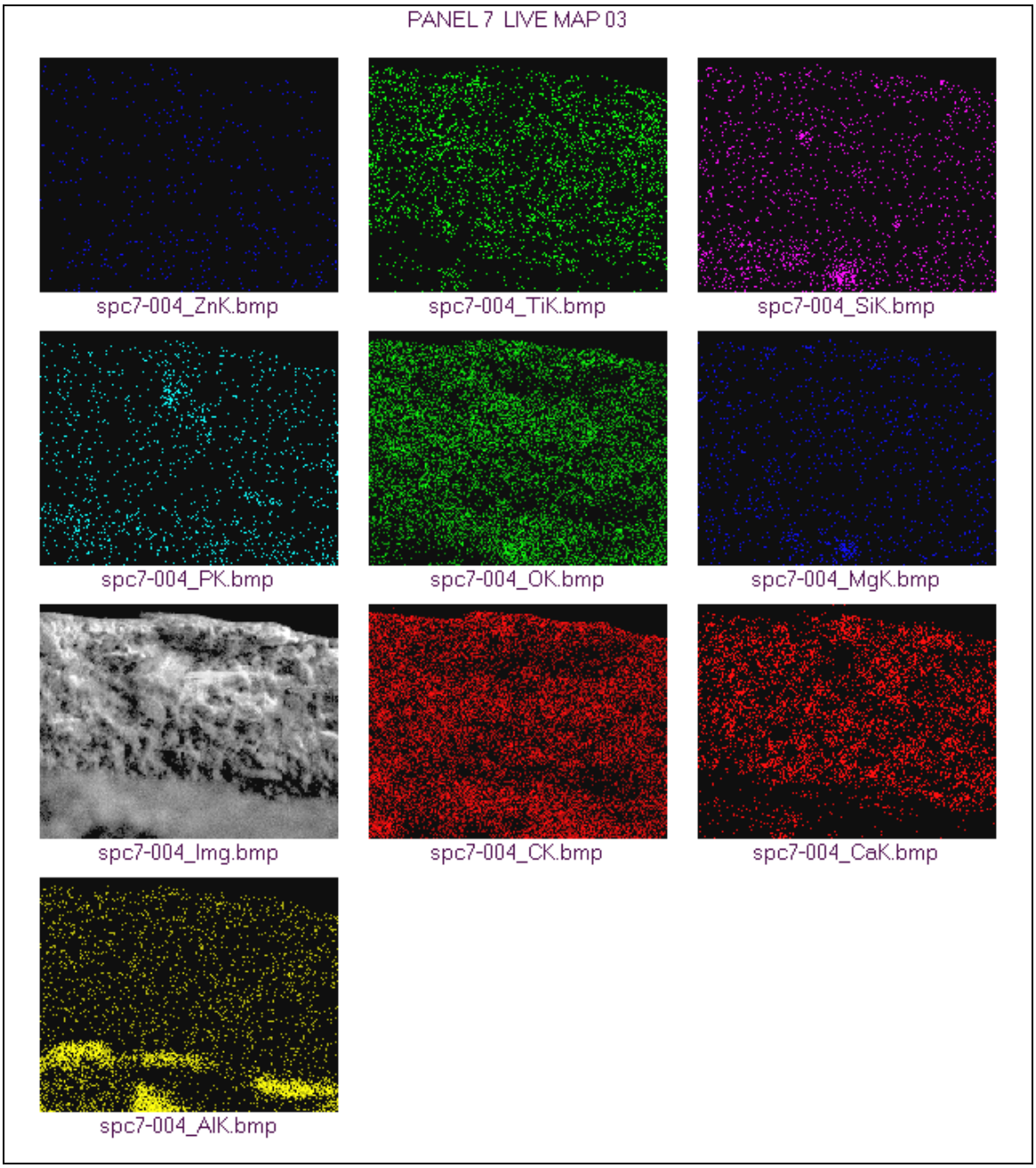

Figure 20. Elemental mapping of panel 7 at 2 KX magnification.

response probably arose from the clip (figures 22 and 23), which was on either side of the film. The film-to-clip contact area was ~2 mm below the surface being examined.

The maps and spectrum shown in figure 24 were collected on a region of the free film away from the clip, so that only the coating was in the beam path (y-axis sample alignment). The emission current could be lowered from 10 to 7 μA and still generate sufficient counts to collect a map with a 360-ms dwell time. In addition, the numerical aperture value was raised from 5.0 to 5.5.

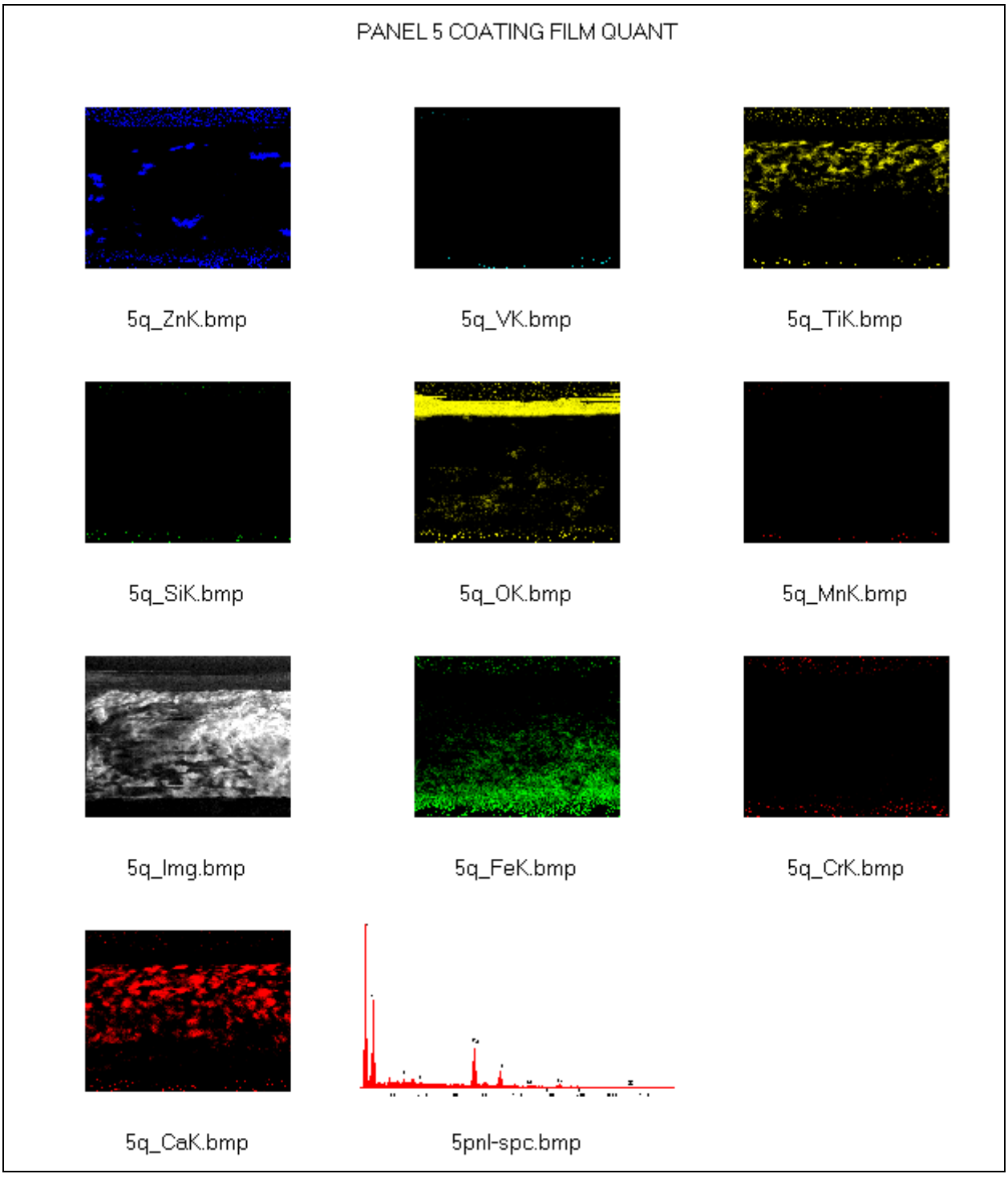

Figure 21. Free film from panel 5. Contrast enhanced for visibility.

Both the Ca K and the Ti K maps are consistent with those in figure 21. The distributions seen in the Zn L, P K, and Na K maps are noteworthy, as they appear to be confined to the right-hand two-thirds of the film thickness. The size of these clusters and the Ca K clusters are significantly different from the Ti K distribution.

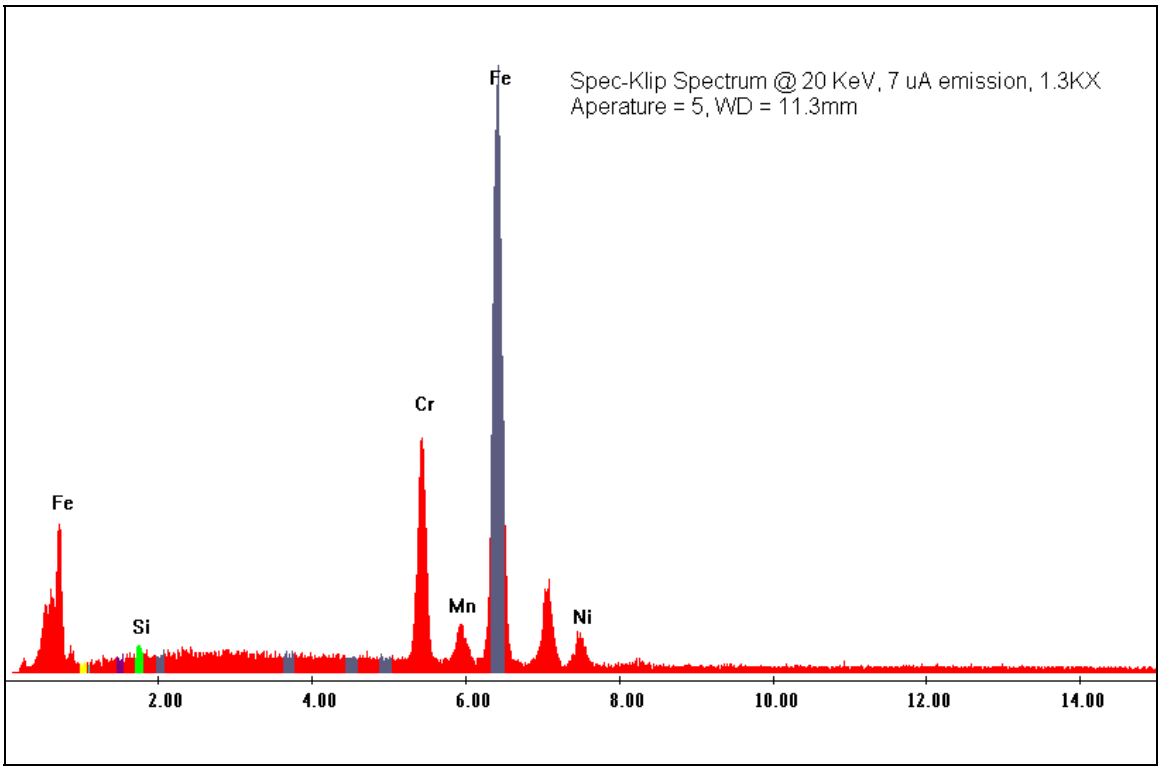

Figure 22. Metal spring clip spectrum.

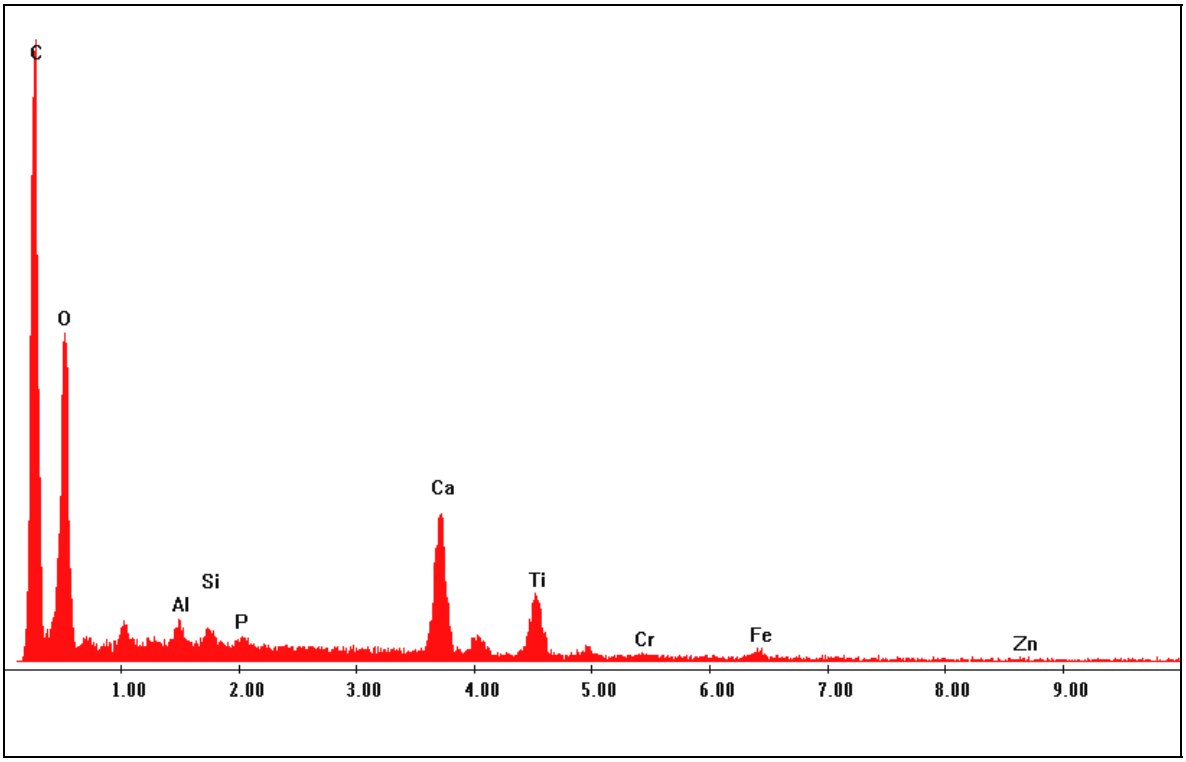

Figure 23. Panel 5 free-film spectrum using Hitachi Live image for alignment.

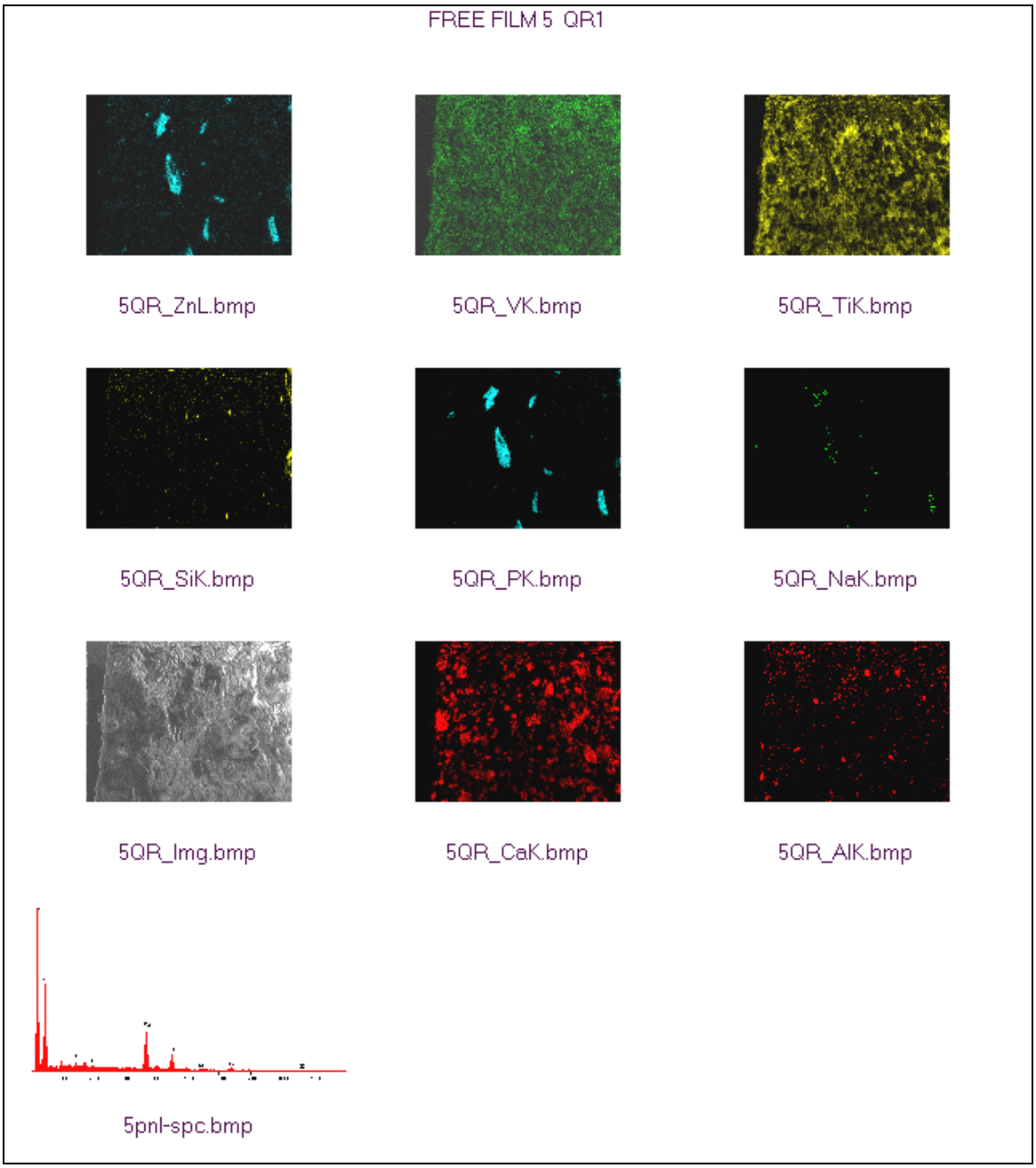

Figure 24. Panel 5 coating free film oriented along the y-axis.

A Live mapping of this same region is shown in figure 25. For the Live mapping the dwell time was 100 ms/256 × 200 pixels frame, and 32 frames were captured. Note the loss of response for the P K peak.

5.2.3 Panel 2 Free Film

The free film from panel 2 was aligned along the y-axis and positioned so that the clip also ran along the y-axis and out of the beam path. Two separate portions of the free film are mapped in

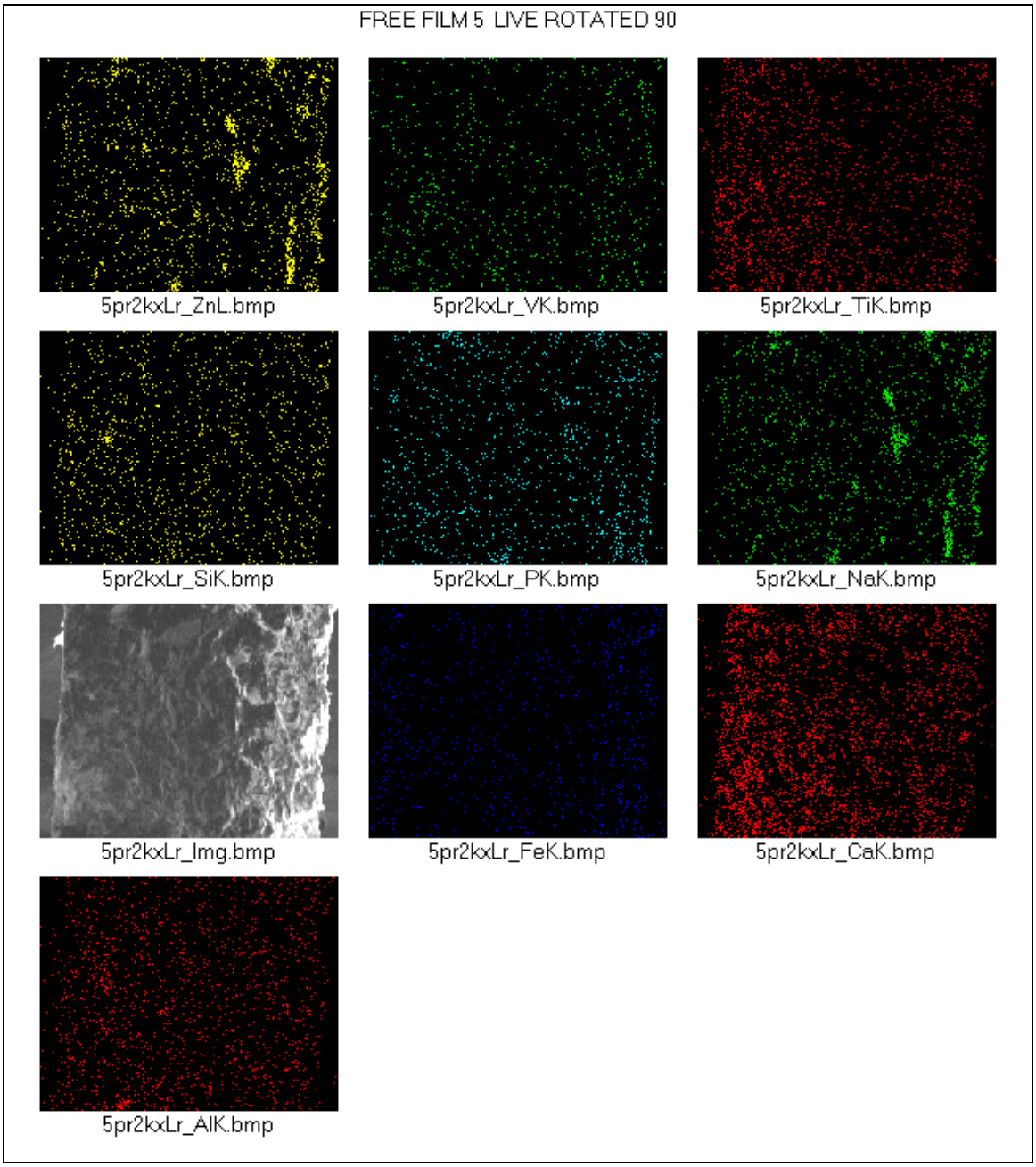

Figure 25. Live mapping of figure 24 region post Quant mapping.

figures 26 and 27. As in the panel 5 free film, the Na, P and Zn maps exhibit large particles in the film.

The differences between figures 26 and 27 arise from the differences in the film geometry at the two sites. The surface plane labeled RAQ faces the EDS detector directly, while the surface plane labeled RBQ slopes off to the right. Note the difference of the Cr K maps between the two sites. The sample was apparently rotated to the apparent 90° position and tilted to expose the left hand image face of the coating. The mappings are mislabeled and reversed. The S-4700 does

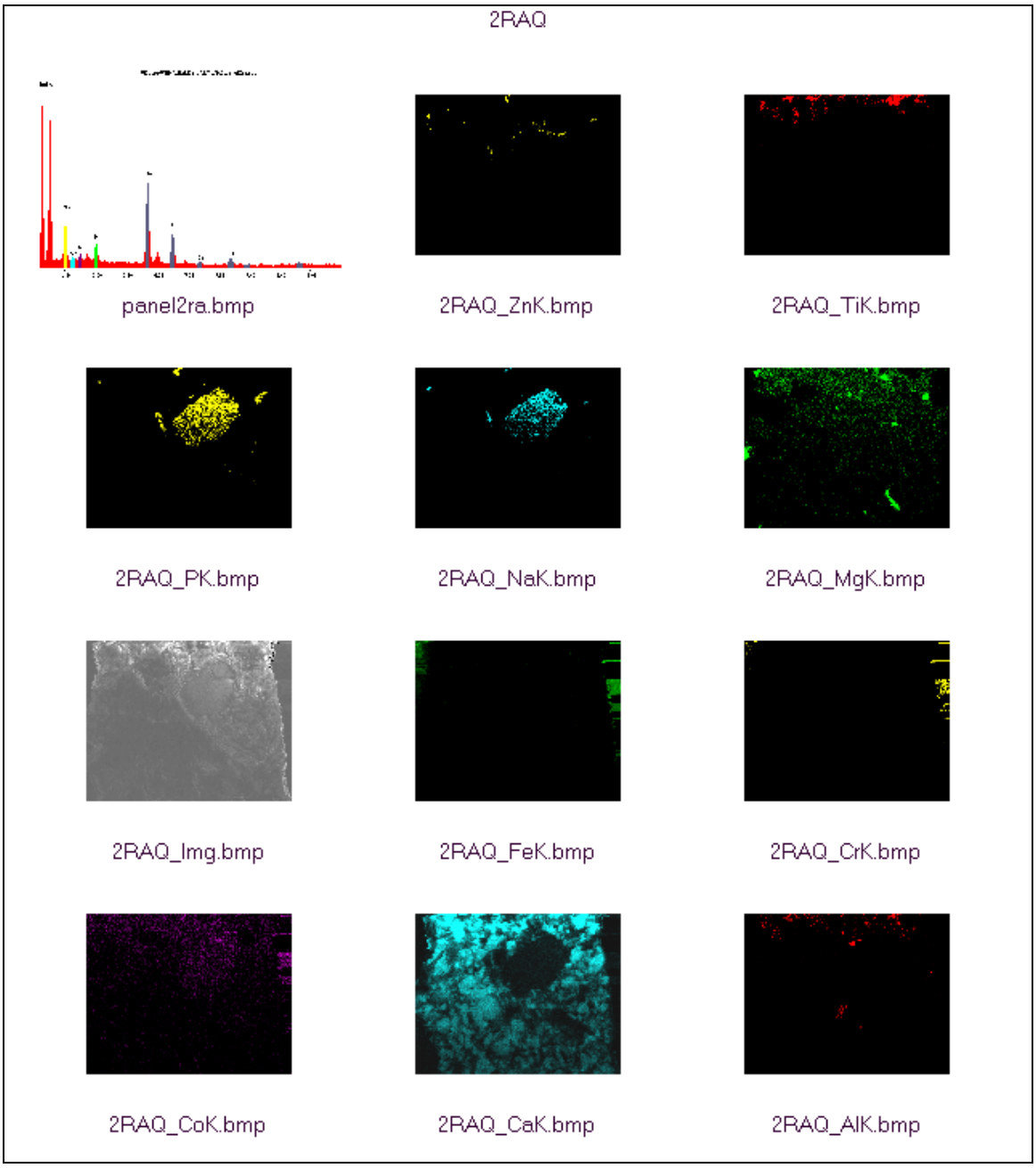

Figure 26. Quant mapping results from panel 2 free film, y-axis alignment.

not correct for image inversion, so the right side in a micrograph is physically the left side on the sample. Figure 28's annotations document the issue. The error was not caught until after the mappings were complete.

The Cr K maps in figures 29 and 30 appear to be similar for each edge. This may be a result of stacking the panels coated face to chromated face. These Live maps don't have sufficient information to identify a panel interface surface (figure 31).

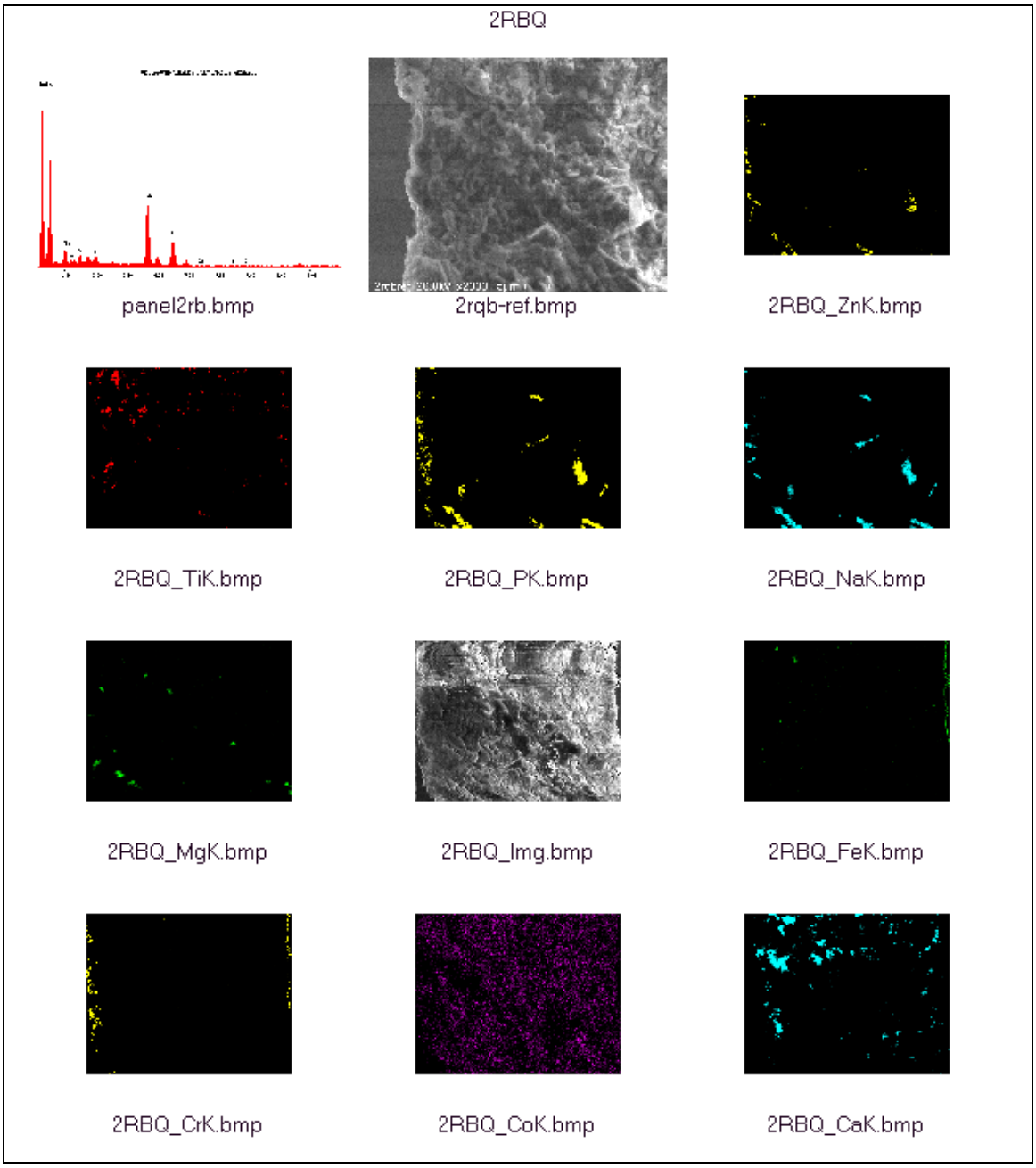

Figure 27. Second Quant mapping of panel 2 free film, y-axis alignment.

5.2.4 Panel 7 EDS Analysis of Coating and Panel

Because of the limitations in positioning the coating on strip from panel 7, it was sectioned by hand. This resulted in two 1.25-in pieces and one 1.5-in piece. The smaller two were mounted individually in spring clips, and then mounted on 13-mm stubs with conductive silver adhesive. The adhesive lacked sufficient strength to bind the 1.5-in section to the stub, so an aluminum micro-vise was used. The micro-vise was a pin mount, requiring an adapter for the S-4700. Both the mechanical fastening to the adapter and the electrical conductivity of the resulting

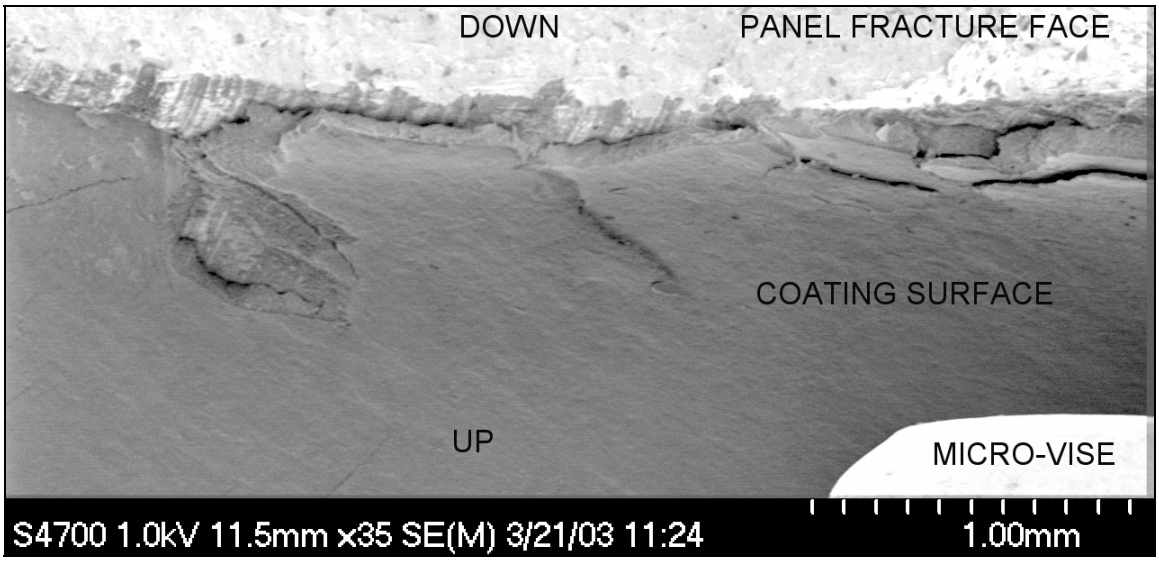

Figure 28. Edge and top surface of strip from panel 7.

mount were insufficient to the required task. One result of this problem is seen in figure 32, where surface charging is obvious on the aluminum micro-vise mount. The emission current was 2 μA, and the numerical aperture value was 5.5.

The physical size of the micro-vise precluded any stage rotation to better position the strip and coating face for examination. The orientation of the sample was restricted to along the x-axis for the same reason. The sample was tilted 20° to better view the coating cross section and aligned with the EDS detector. The ideal tilt angle of 30° was not possible due to the same size issue. Because of the invert image, the coating on panel 7 appears to be under the panel and tilting up toward the observer (figure 28). In reality, the coating is on top, tilted down toward the observer, and the coating cross section is aligned with the EDS detector window. The alignment was done using the internal charged couple device (CCD) camera of the S-4700.

In figure 33, note the Al K map and then the distributions seen in the Zn L and P K maps. For panel 7, the Zn P inclusions are closely associated with the panel coating interface area, indicating the primer chemical and physical distributions. This primer was applied to all the panels at the same time. No distinct chromium layer or peak visible.

Finally, a spectrum and a Quant map were taken of the aluminum fracture face of panel 7 (figure 34). The panel with coating spectrum and the panel spectrum are presented in figure 35 for comparison.

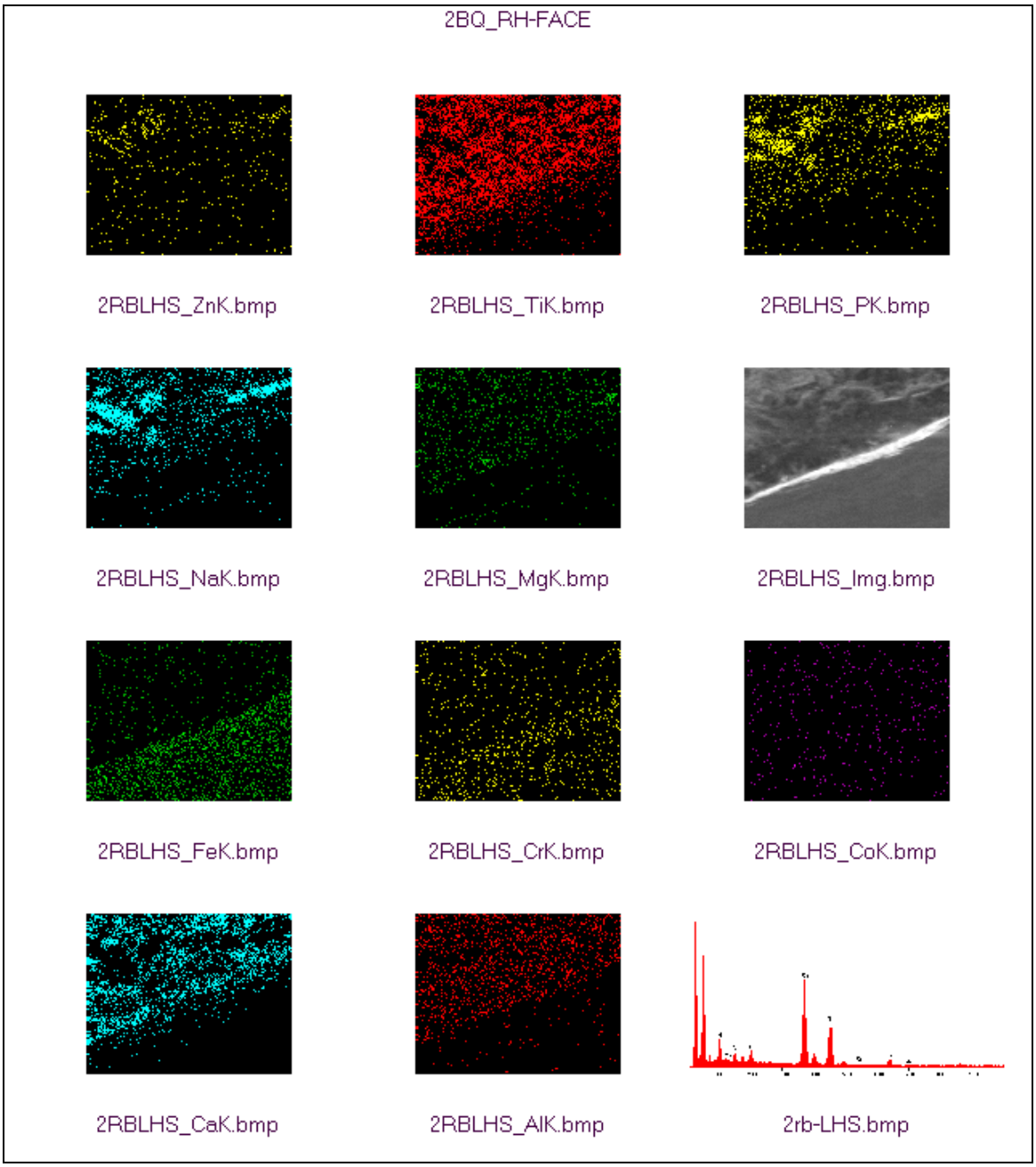

Figure 29. Live elemental map of right-hand face of panel 2 free film, mapped at 20-KeV, 2-KX, and 100-ms dwell time.

6. Conclusion

Quantitative elemental mapping of the three coating films and aluminum substrate indicate the presence of a primer layer thicker than that required by the application, but no distinct chromate wash primer layer was seen. Because of the random surface charging on all the samples, a full

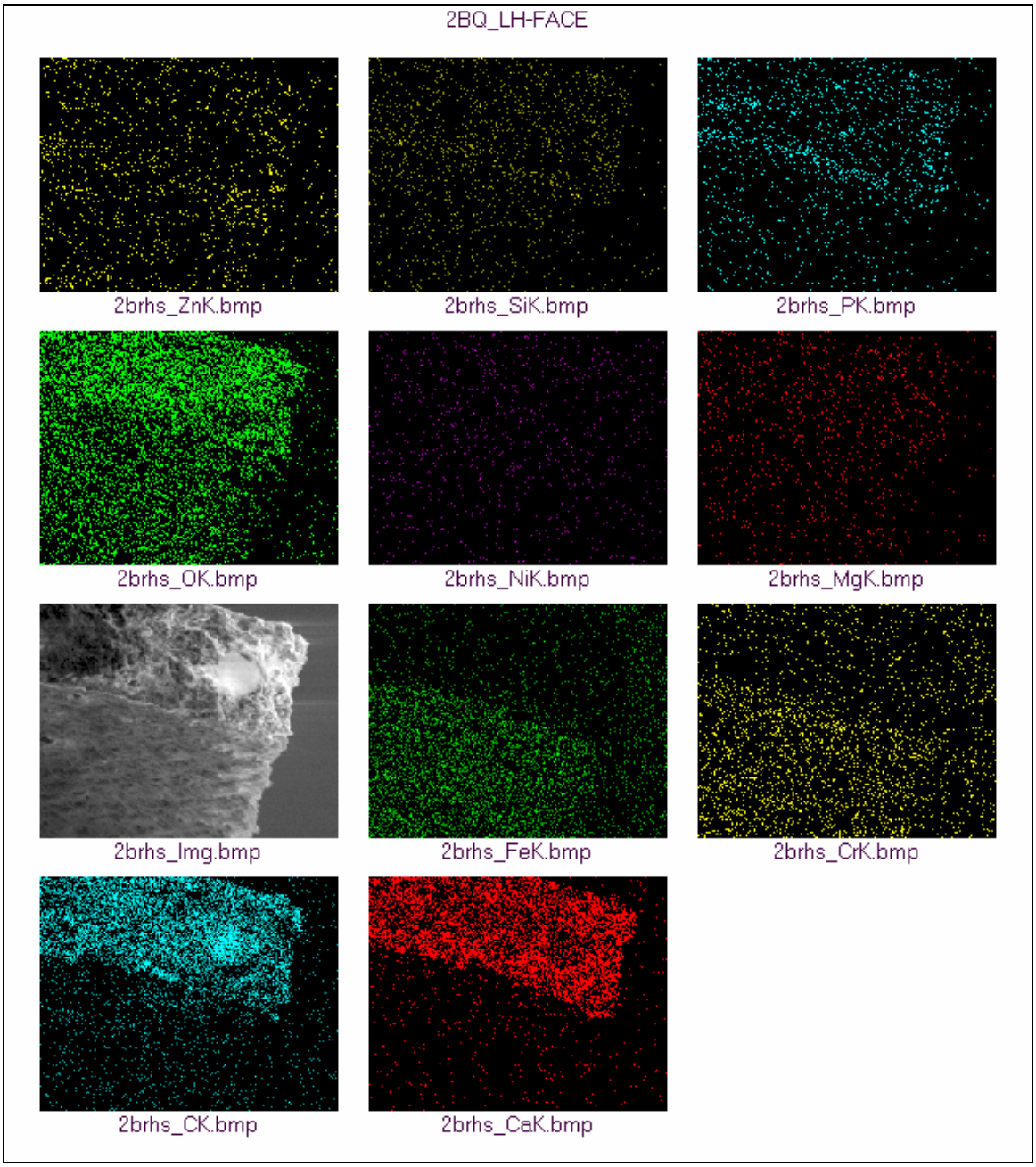

Figure 30. Live elemental map of panel 2 free film, left-hand face at 20-KeV, 900×, and 125-ms dwell time.

quantization could not be achieved, but the relative results are more than sufficient to determine the thickness of the primer layers. All three films show the presence of large Zn/Na P inclusions, preferentially distributed to one side of the film. The mappings of panel 7 and its coating provide compelling evidence that the first primer layer applied is the main area for those inclusions. It is reasonable to assume that the Zn P mappings seen in the free films from panels 2 and 5 lie primarily within the primer layer, making the primer accountable for about two-thirds

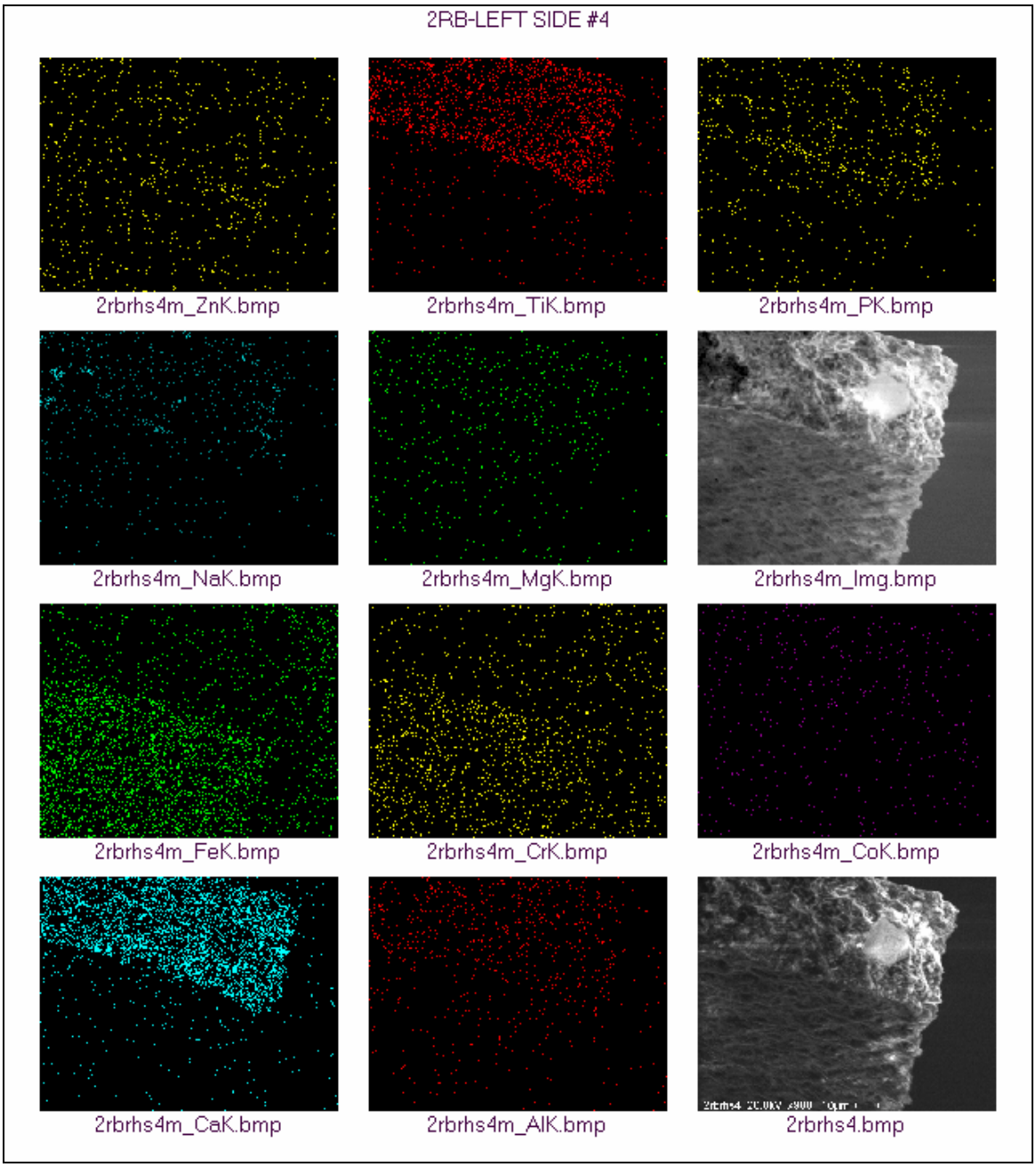

Figure 31. Repeat of Live elemental map from figure 29.

of the film thickness in all instances. The large aggregations of the ZN/Na P inclusions are not normal, occur frequently for the small area sampled, and may be the source of the blistering observed.

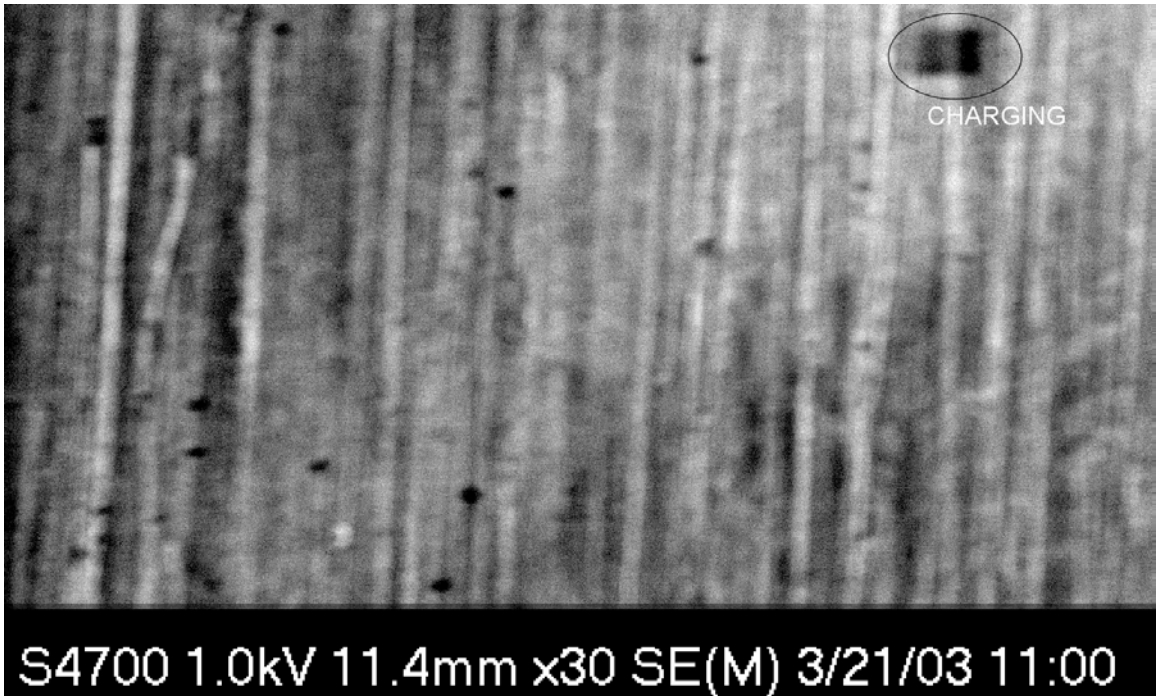

Figure 32. Surface charging on surface of aluminum micro-vise.

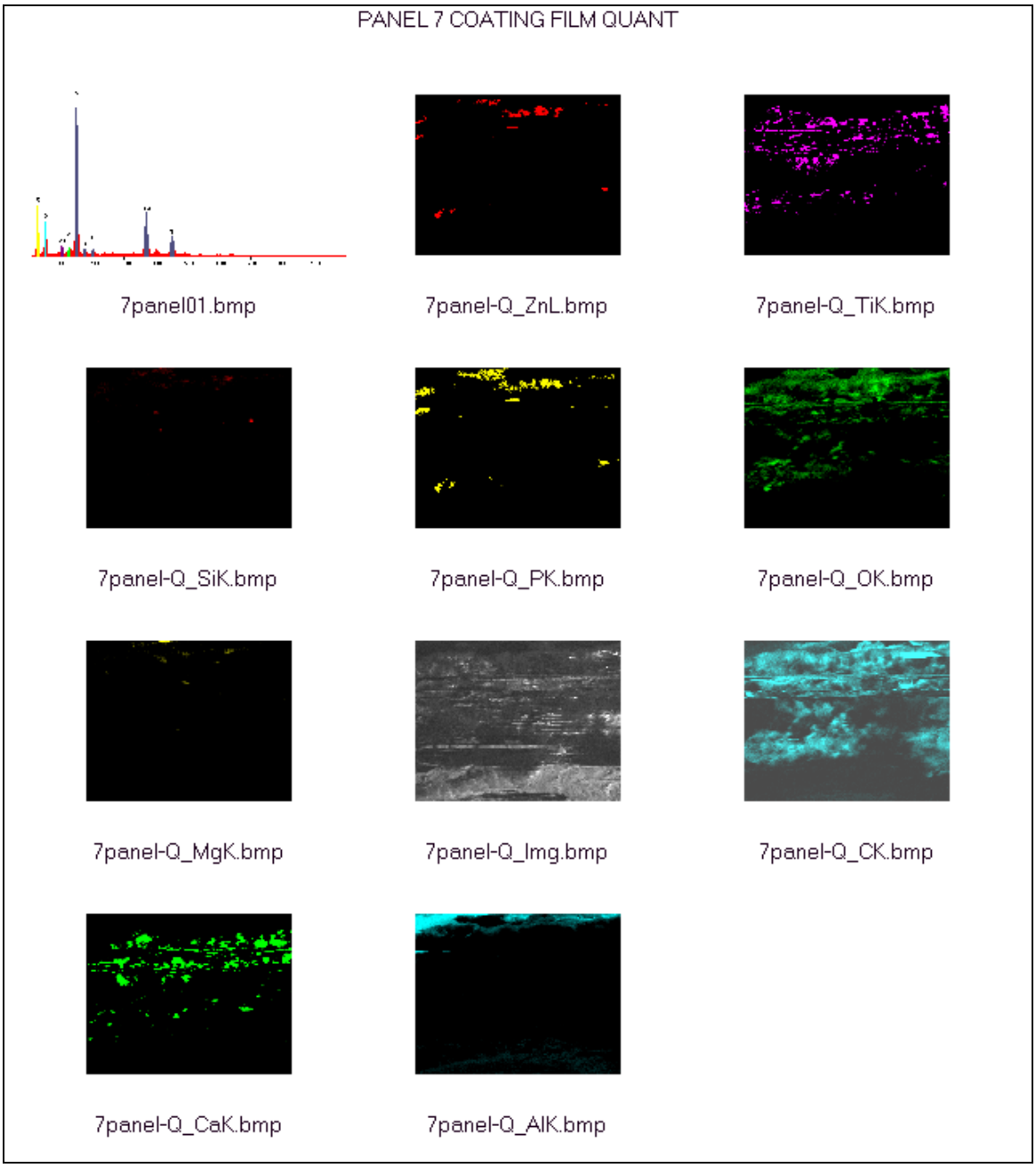

Figure 33. Elemental map of panel 7 coating cross section.

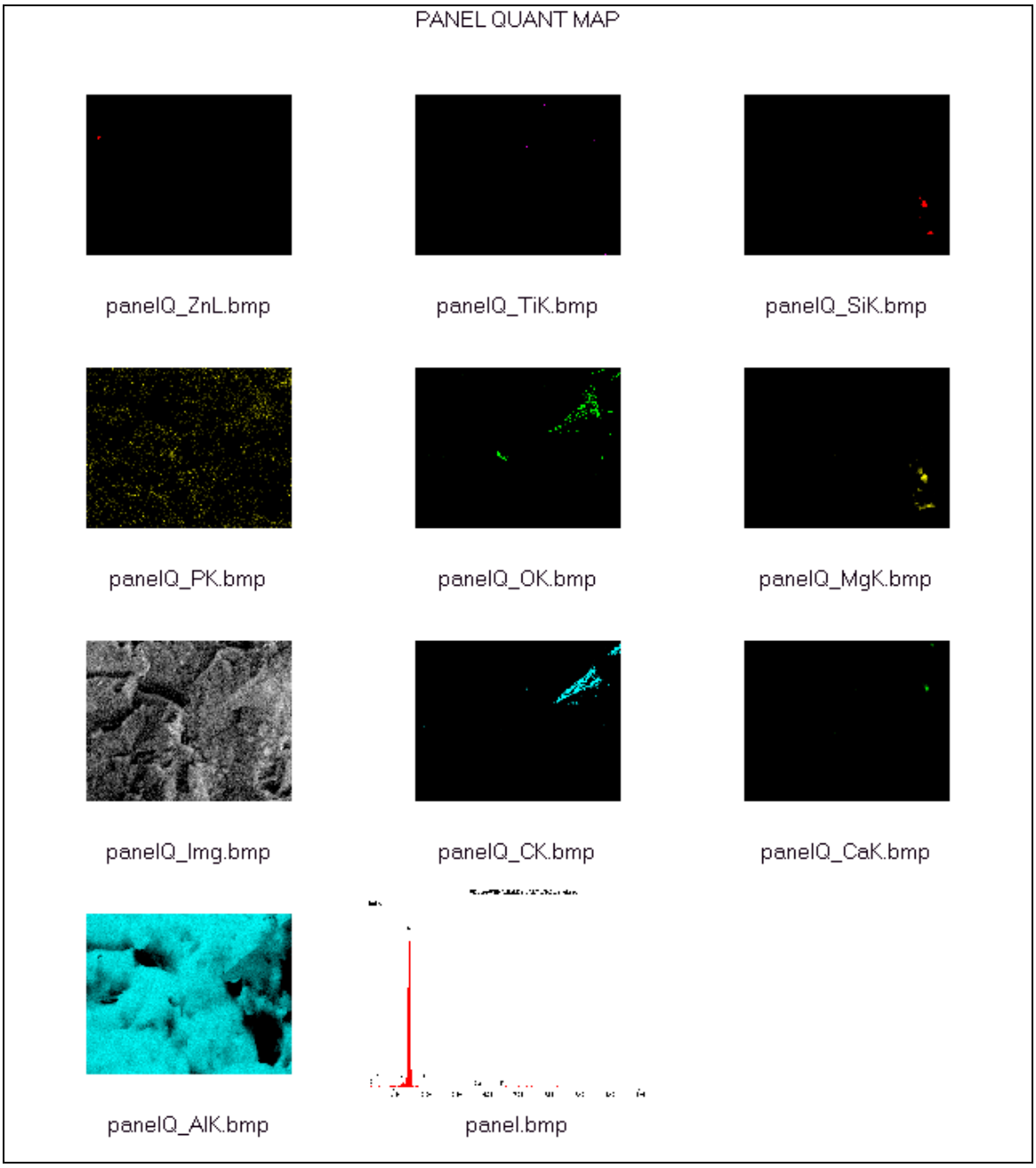

Figure 34. Elemental mapping of the fracture face from panel 7.

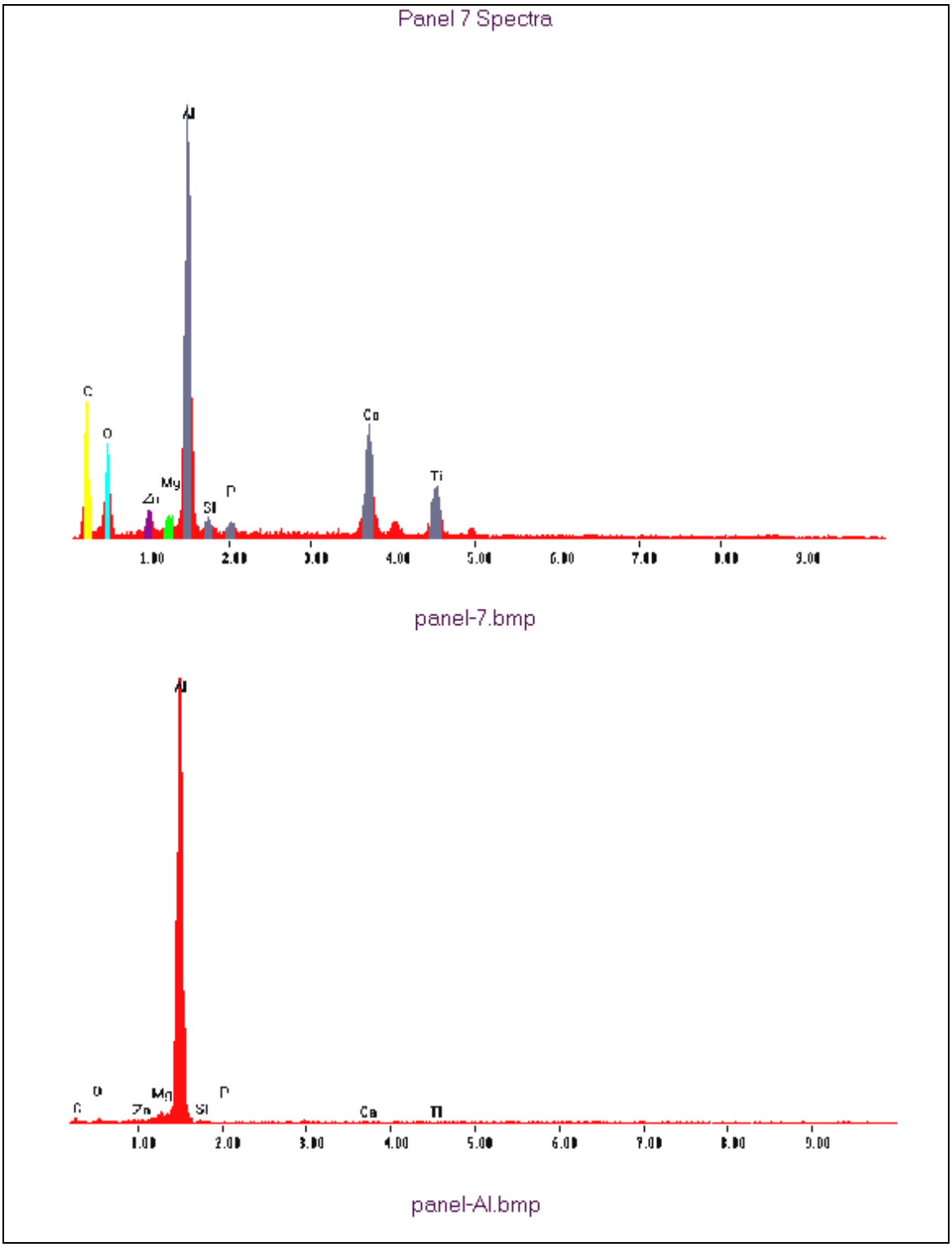

Figure 35. Panel 7 reference spectra.

List of Symbols, Abbreviations, and Acronyms

CCD	Charged couple device
EDS	Energy dispersive spectrometer
eV	Electron volt
FE-SEM	Field emission-scanning electron microscope
KeV	1000 eV
#KX	#,000× magnification
ms	Millisecond
SE	Secondary electron
μA	Microampere
YAG	Yttrium aluminum garnet
YAGBSE	Yttrium aluminum garnet backscatter detector

EDS Spectra Abbreviations

Al K	Aluminum K emission line
C K	Carbon K emission line
Ca K	Calcium K emission line
Cr K	Chromium K emission line
Fe K	Iron K emission line
Mg K	Magnesium K emission line
Mn K	Manganese K emission line
Na K	Sodium K emission line
O K	Oxygen K emission line
P K	Phosphorous K emission line
Si K	Silicon K emission line
Ti Kβ	Titanium K beta emission line
V K	Vanadium K emission line
Zn K	Zinc K emission line
Zn L	Zinc L emission line
K	K atomic shell
L	L atomic shell
ZAF	Atomic number **Z**
	X-ray absorption **A**
	X-ray fluorescence **F**

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